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DEVELOPMENT AND APPLICATION OF TECHNIQUES FOR PREDICTING LEACHATE QUALITY IN CONFINED DISPOSAL FACILITIES

BACKGROUND AND THEORY

by

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A theoretical framework for predicting leachate quality in confined disposal facilities was developed using mass transport theory. The physical-chemical processes governing leaching were identified and described mathematically.

Various approaches to describing contaminant transfer from the dredged material solids to the aqueous phase were considered, including equilibrium concepts, dissolution kinetics, intraparticle diffusion, and film effects. The approach recommended for application to dredged material uses an operationally defined distribution (partitioning) coefficient to relate aqueous phase concentration to solid phase concentration. This approach assumes equilibrium within the dredged material between solid and aqueous phases. The equilibrium approach assumes that interphase transfer kinetics are fast compared to the percolation rate of water through dredged material.

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The theoretical analysis was used to design laboratory tests for determining the leaching characteristics of dredged material. A sequential batch leach test is recommended for obtaining distribution coefficients, and a pressurized column test using divided-flow (double-ring) permeameters is recommended as a physical model of reduced scale for verifying the distribution coefficients obtained in batch tests. The design concepts for the laboratory tests are preliminary, and additional evaluation on the basis of actual test results will be needed before the procedures recommended can be adopted.

SUMMARY

Predictive techniques for leachate quality and generation rates have not been practical for dredged material, largely due to the fact that the basic processes governing leaching are poorly understood. The specific objective of this report is to provide the theoretical framework for developing predictive techniques for leachate quality in confined disposal facilities for dredged material.

A theoretical framework was developed on the basis of mass transport theory. By applying the principles of mass transport theory, the physical-chemical processes governing leaching were identified and described mathematically. A review of selected literature on the leaching of contaminated sediments was used to identify important factors specific to dredged material. A laboratory program including batch and column leach tests was designed on the basis of the theoretical analysis and the literature review. The design concepts are preliminary, and additional evaluation on the basis of actual test results will be needed before the procedures recommended can be adopted.

A one-dimensional mass transport equation was developed for analyzing contaminant transport in a dredged material confined disposal facility. The equation combines convective-diffusive transport with a source term for leaching of contaminants from dredged material solids. Various approaches to describing the fundamental processes controlling contaminant transfer from the dredged material solids to the aqueous phase were considered, including equilibrium concepts, dissolution kinetics, intraparticle diffusion, and film effects. The approach recommended for application to dredged material uses an operationally defined distribution (partitioning) coefficient to relate aqueous phase concentration to solid phase concentration. This approach assumes equilibrium within the dredged material between the solid and aqueous phases. The equilibrium approach is justified on the basis that interphase transfer kinetics are fast compared to the percolation rate of water through the dredged material profile.

State-of-the-art leaching procedures were reviewed for potential application to dredged material. Various topics related to sediment chemistry impacts on leaching processes were also reviewed. A sequential batch leaching procedure is recommended for obtaining the coefficients needed in the mass transport equation. In order to verify the equilibrium assumption and the

mass transfer equation, a pressurized column test using divided-flow (double-ring) permeameters is recommended as a physical model of reduced scale.

PREFACE

This report was prepared by Dr. Donald O. Hill, Department of Chemical Engineering, Mississippi State University, and Mr. Tommy E. Myers and Dr. James M. Brannon, Environmental Laboratory (EL), US Army Engineer Waterways Experiment Station (WES), for the Office, Chief of Engineers (OCE), US Army, through the Dredging Division of the Water Resources Support Center (WRSC-D), Fort Belvoir, Va. Funds for publication of this report were provided by the Dredging Operations Technical Support (DOTS) Program. The DOTS Program is managed within EL's Environmental Effects of Dredging Programs, Dr. Robert M. Engler, Manager, and Mr. Thomas R. Patin, DOTS Coordinator. The Technical Monitor for DOTS was Mr. Dave Mathis, WRSC-D.

Review and constructive comments were received from a technical working group assembled at the WES. Participants included Dr. Brannon, Mr. Norman R. Francingues, Jr., Mr. Jerry N. Jones, and Mr. Myers, EL; Dr. Gary Goforth, Florida Water Resources Research Center, University of Florida; Dr. David B. Grove, Water Resources Division, US Geological Survey, Denver, Colo.; Dr. Hill, Mississippi State University; Dr. Samuel W. Karickhoff, Environmental Research Laboratory, US Environmental Protection Agency (USEPA), Athens, Ga.; Dr. Duane E. Long, Analytical Systems Division, US Army Dugway Proving Ground, Dugway, Utah; Mr. Charles Mashni and Dr. Mike H. Roulier, Hazardous Waste Engineering Research Laboratory, USEPA, Cincinnati, Ohio; Dr. William H. Patrick, Jr., Center for Wetlands Resources, Louisiana State University; and Dr. Hans Van der Sloot, Netherlands Energy Research Foundation, The Netherlands.

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CONTENTS

	Page
SUMMARY	1
PREFACE	3
PART I: INTRODUCTION	6
Scope	6
Objectives	7
PART II: APPROACH	8
Mathematical Description	9
Research Needs	11
PART III: BACKGROUND REVIEW	13
Equilibrium Processes	13
Nonequilibrium Processes	22
PART IV: PREDICTION OF CONTAMINANT LEACHING FROM DREDGED MATERIAL	37
Application of Transport Theory	37
Factors Influencing Contaminant Mobility in Dredged Material	39
PART V: LABORATORY PROCEDURES FOR INVESTIGATING CONTAMINANT MOBILITY IN DREDGED MATERIAL	45
Current Testing Procedures	45
Recommended Test Procedures	51
PART VI: SUMMARY	57
REFERENCES	58
APPENDIX A: DERIVATION OF ONE-DIMENSIONAL MASS TRANSPORT EQUATION	A1
APPENDIX B: FUGACITY BASIS FOR EQUILIBRIUM DISTRIBUTION COEFFICIENTS	B1
APPENDIX C: DEVELOPMENT AND USE OF ADSORPTION ISOTHERM EQUATIONS	C1
Freundlich Isotherm	C1
Langmuir Isotherm	C2
BET Isotherm	C4
APPENDIX D: DEVELOPMENT AND USE OF DESORPTION ISOTHERM EQUATIONS	D1

DEVELOPMENT AND APPLICATION OF TECHNIQUES FOR PREDICTING LEACHATE QUALITY IN CONFINED DISPOSAL FACILITIES

BACKGROUND AND THEORY

PART I: INTRODUCTION

1. Contaminated dredged material is sometimes disposed in confined disposal facilities (CDF's) designed and operated to control environmental impacts. When contaminated dredged material is placed in a CDF, contaminants may be mobilized and transported to the site boundaries by leachate generation and seepage. Subsurface drainage and seepage through dikes may then reach adjacent surface and ground waters and act as a source of contamination. Since the contaminants present in dredged material are adsorbed to sediment particles, leaching by percolating site water is the primary mechanism by which contaminant migration to ground water takes place. Other mechanisms that can be involved in contaminant migration are volatilization, surface runoff, plant uptake, and other forms of biologically mediated transport.

2. Proposed changes in implementation of Section 404 of Public Law 95-217, as amended, call for a more detailed evaluation of the confined disposal alternative to include leachate quality and ground-water impacts. At present there is no routinely applied laboratory testing protocol capable of predicting leachate quality from CDF's. Techniques for predicting leachate quality in CDF's are needed to establish sound engineering and environmental data for the selection, design, and management of CDF's. A detailed technical approach and rationale for testing and evaluating the leaching potential of dredged material is presented in this report.

Scope

3. This document develops and critically examines a procedure for providing planning level assessments of leachate quality in a CDF. Included is a review of pertinent literature and a recommended procedure for evaluating the pollutant potential of contaminated dredged material.

Objectives

4. The objective is to provide a detailed technical approach for developing techniques for predicting leachate quality in CDF's. Specific supporting objectives are as follows:

a. To provide a review of selected literature on leaching of contaminated materials.

b. To derive, from the principles of transport theory, the physical-chemical processes that govern the movement and leaching of contaminants from dredged material.

c. To identify specific factors that should be considered in developing a leaching test for contaminated dredged material.

d. To identify appropriate experimental methods and required interpretative protocols for predicting the leaching potential of contaminated dredged material.

PART II: APPROACH

5. A thorough understanding of the probable behavior of dredged material in a CDF is necessary to make judgments as to the effectiveness of the contaminant containment provided by these facilities. Generally speaking, such an understanding may be gained in one of two ways. The first is to use an empirical approach whereby information is obtained through experience rather than theoretical analysis. This approach requires long-term experience with data from many types of facilities to identify the critical factors influencing the results. Statistical correlations can be useful when correctly applied to systems fundamentally similar to those from which the data were collected. However, approaches based solely on statistics have no physical basis, and extrapolation outside the range of observation is rarely justified.

6. An alternative approach is to mathematically describe the system using equations developed from fundamental principles applicable to all physical systems. The major advantage of this approach is that once the derived equations have been experimentally verified, they can be used outside the range of experimentation (Stanislav 1982). This means that long-term predictions can be made on the basis of minimal data. Sometimes the complexities of a given problem are such that a quantitative description of all aspects cannot be derived from fundamental principles. In these situations, some combination of theory and experimentation is needed to provide a better understanding of process mechanisms.

7. The approach taken in this report is to derive as many quantitative relationships for contaminant leaching in CDF's as possible from the principles of transport phenomena and to indicate where additional experimentation is needed. Studies involved with transport phenomena of natural systems use partial differential equations that are known as the "equations of change." The reader is referred to Bird, Stewart, and Lightfoot (1960) for a detailed presentation of these equations and to Thibodeaux (1979) for a comprehensive treatment of how these equations can be applied to environmental problems. The mass transport equation appropriate for the study of dredged material is given in the following section. The development of this equation gives rise to a source term that will be of particular importance to this report and will be given detailed attention.

Mathematical Description

8. A small volume of material within a confined dredged material site is shown in Figure 1. This volume element receives a contaminant flux from the upper layer and discharges a contaminant flux to the layer below the element. The mass flux in and out of the element may be described by a material balance on the volume element. For the z direction, the one-dimensional mass transport equation is as follows (Hornsby and Davidson 1973, Lowenbach 1978, Rao et al. 1979, Grove and Stollenwerk 1984):

$$D_p \frac{\partial^2 C_i}{\partial z^2} - v \frac{\partial C_i}{\partial z} + S = \frac{\partial C_i}{\partial t} \tag{1}$$

$$S = - \frac{\rho}{\theta} \left(\frac{\partial q}{\partial t} \right) \tag{2}$$

where

D_p = dispersion coefficient for i^{th} contaminant, L^2/t

t = time

C_i = aqueous phase concentration of i^{th} contaminant, m/L^3

z = space dimension, L

v = average pore water velocity, L/t

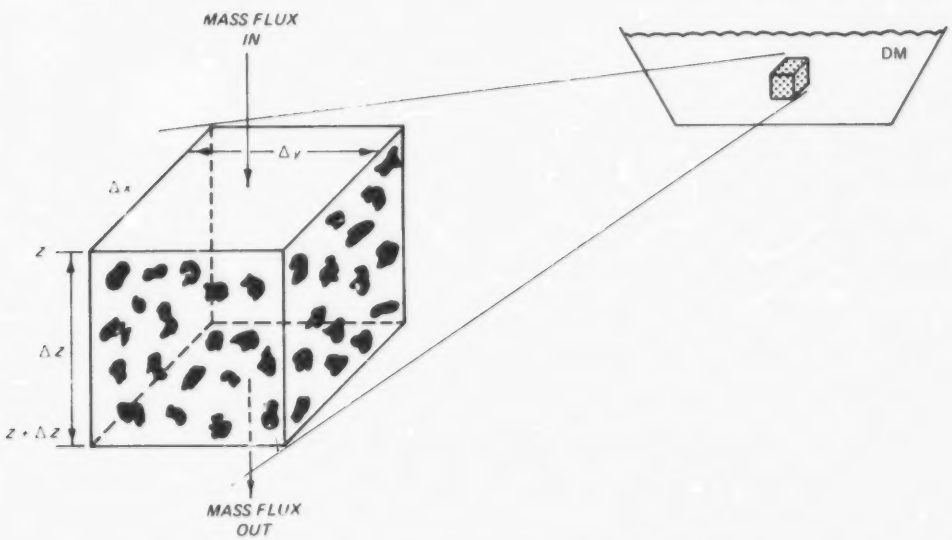

Figure 1. Incremental element of dredged material (DM) from a typical containment area

S = source term for contaminant leaching, m/L^3t

ρ = bulk density, m/L^3

θ = volumetric water content, L^3/L^3

q = solid phase contaminant concentration, m/m

Equation 1 is the materials balance for the aqueous phase (pore water), and Equation 2 is the materials balance for the solid phase. Equation 2 defines the source term in Equation 1 as the rate of transfer between solid and aqueous phases. Thus, there are two component balances, one for each phase, that must be solved simultaneously. The derivation of Equation 1 is given in Appendix A.

9. Equations 1 and 2 provide a theoretical framework for the development of a predictive model. Given certain assumptions, initial conditions, and boundary conditions, Equation 1 can be used to develop planning-level assessments of contaminant mobility in a CDF. In particular, impacts on ground water immediately beneath the site can be evaluated. The first term represents dispersive transport of aqueous phase contaminants; the second term represents convective transport. The source term describes the rate of contaminant transfer between the solid and aqueous phases. It should be noted that similar expressions could be written for the other two space dimensions (Lowenbach 1978). However, it is anticipated that the one-dimensional approach will adequately assess the pollutant potential of dredged material in CDF's.

10. In the definition sketch presented in Figure 1, an element within the containment site is shown. The segment of the CDF under consideration can be extended from the air interface through the dredged material proper, through any liner material that may be present, and into the region of the water table by dividing the disposal facility into a number of discrete elements in the vertical. As water percolates through the containment area and into the soil below, the migration of contaminants that accompanies the percolation of water through the site can be predicted by applying the mass transport equation to each element. In this fashion, changes in the properties of materials between elements can be accounted for.

11. Even though the above visualization makes the problem appear simple, it is indeed very complex. A major problem with predictive techniques of this type lies with the development of the needed data, especially data for the

source term. The bulk flow term also presents problems during the period of active consolidation and when unsaturated flow characterizes the system.

Research Needs

12. Predictive techniques based on mass transport equations such as Equations 1 and 2 have not been practical for dredged material, largely due to inadequate information for the source term. A comprehensive theory that describes the leaching of sediment solids has not been developed, and basic processes are poorly understood. Without an adequate theoretical base, it has not been possible to design laboratory leach tests with a sound technical basis for extrapolation to the field situation.

13. The predictive protocol developed in this report is based on the use of Equations 1 and 2. In order to apply Equation 1 as a predictive tool, certain information for each term is needed. Development of this information requires laboratory testing. Laboratory procedures are available for obtaining coefficients for the bulk flow and dispersion terms in the equation, but procedures are not available for quantifying the contaminant source term.

14. For the bulk flow term in Equation 1, $v(\partial C/\partial z)$, seepage velocity data must be developed. Velocity under saturated conditions can be treated as steady flow using Darcy's equation. As the sediments consolidate and the site dries out, the flow regime may become unsaturated. Unsaturated flow processes are, in general, complicated and difficult to model. Recent advances, however, provide state-of-the-art numerical models that can be used to model the unsaturated flow regime. Water flow through the dredged material will be greater, however, under saturated flow conditions. Saturated flow conditions, therefore, represent a "worst-case" flow situation. For the predictive techniques developed in this report, a worst-case flow situation, saturated flow, is assumed to prevail in the CDF.

15. As dredged material in a CDF consolidates, pore water is forced out. Some of the pore water rises and pools in the CDF, some may move laterally through the dikes, and some may move downward, depending on the hydraulic gradient and the hydraulic conductivity of the dredged material and the foundation material in the disposal facility. As consolidation proceeds, the hydraulic conductivity of the dredged material decreases. This is particularly important during the early stages of consolidation. The predictive

techniques developed in this report apply to dredged material for which consolidation is essentially complete. The general approach, however, can be extended to include the period of active consolidation by taking into account changes in porosity, bulk density, and seepage velocity as a function of consolidation.

16. Dispersive transport is represented in Equation 1 by $D_p(\partial^2 C/\partial^2 z)$. Dispersive transport is the result of two processes, mechanical mixing and diffusion (Javandel, Doughty, and Tsang 1984). Mechanical mixing is the result of velocity variations within the porous medium. Diffusion is the process whereby ionic and molecular constituents move under the influence of concentration gradients. The dispersion coefficient, D_p, is the sum of the effective molecular diffusion coefficient, $\bar{D}$, and the product of the velocity and the characteristic dispersive length, α (Freeze and Cherry 1979; Javandel, Doughty, and Tsang 1984). Thus, D_p is given by

$$D_p = \alpha v + \bar{D} \tag{3}$$

Laboratory methods are available for determining dispersion coefficients (Levenspiel 1972, Goerlitz 1984).

17. With procedures available for obtaining information on dispersive and convective flux, the only term left in Equation 1 that needs standard procedures for quantifying is the source term. Initially, the sediments in a CDF will be saturated, and there will be only two phases (aqueous and solid) for the source term to describe. (As the site dries out, the gas phase can become important.) It should be realized that without the source term, there is no transfer of contaminants from the sediment to the leachate. The source term is an essential part of the mass transport equation and is central to the development of a predictive protocol. Adequate description of the source term may require consideration of thermodynamics (equilibrium processes), kinetics, and local mass transfer principles. These processes are discussed in PART III. In order to assess long-term environmental impacts from dredged material sites, the source term must also be described in terms of changing environmental conditions in the CDF. Environmental conditions affecting contaminant mobility in dredged material are discussed in PART IV. The objective of the laboratory program recommended in PART V of this report is to develop an accurate description of the source term.

PART III: BACKGROUND REVIEW

18. This background review will examine the application of transport theory to contaminant mobility in dredged material. Concepts from thermodynamics (equilibrium), kinetics, and mass transfer and their application to quantification of the source term in Equation 1 are considered. Sorption fundamentals that apply to dredged material are treated in detail.

19. Transport processes may be classified as equilibrium processes or nonequilibrium processes. Equilibrium processes are controlled by thermodynamics and may involve mass transfer, while nonequilibrium processes involve reaction kinetics and mass transfer (Bird, Stewart, and Lightfoot 1960, Thibodeaux 1979, Geankoplis 1983). Consequently, it is necessary to involve all three areas in this discussion of contaminant leaching.

Equilibrium Processes

20. In closed systems, chemical equilibrium is a dynamic process in which species are being adsorbed and desorbed concurrently and reversible reactions proceed in both directions (reactants to products and products to reactants). At equilibrium there is no net change in chemical potential (Thibodeaux 1979). In open systems, equilibrium involves steady-state mass transfer. The following discussion addresses adsorption/desorption equilibria.

Distribution (partitioning) coefficients

21. The present discussion pertains to equilibrium processes at the interface between sediment and water. The sediment/water interface is defined as the place at which the solid phase and the aqueous phase meet and interact. A contaminant introduced on one side of the interface will move across the interface until equilibrium is established. At equilibrium, the contaminant is distributed or partitioned between the two phases so that the chemical potentials in the solid and aqueous phases are equal (Thibodeaux 1979). Equilibrium considerations for dredged material leaching involve interphase equilibria for gas, aqueous, and solid phases. Depending on the degree of saturation in a CDF, various interphase equilibria may be present.

22. For saturated, steady-state flow, there will usually be only one equilibrium to consider, the sediment/water equilibrium. If the rate of contaminant transfer across the sediment particle/pore water interface is

rapid relative to the convective and dispersive transport in the pore water, then for all practical purposes, chemical equilibrium exists between pore water and sediment particles. In this case the leaching process will be equilibrium controlled, and distribution coefficients can be used to describe the source term. In unsaturated flow, in addition to a sediment/water equilibrium, gas/water/sediment equilibria may also be important for certain substances. Gas/solid equilibria will be relatively unimportant except in dredged material layers with low water content, such as the surface crust.

23. Thibodeaux (1979) and Mackay (1979) have suggested that the fugacity concept be used in place of chemical potentials to develop equilibrium distribution coefficients. (See Appendix B for a discussion of distribution coefficients.) From a consideration of aqueous and solid phase fugacities at equilibrium, the following distribution coefficient can be derived:

$$K_d = \frac{W_{i3}}{W_{i2}} \tag{4}$$

where W_{i3} is the mass fraction of the i^{th} chemical contaminant in the sediment and W_{i2} is the mass fraction of the i^{th} chemical contaminant in the aqueous phase. (Note that the subscript 2 refers to the aqueous phase and the subscript 3 refers to the solid phase.) Equation 4 is derived in Appendix B. This equation can be used to relate aqueous phase contaminant concentration to the solid phase contaminant concentration through the use of a simple distribution coefficient if the following conditions are satisfied:

a. The sediment/water system approaches steady state.

b. The solid phase contaminant concentration is much less than the ultimate adsorption capacity of the sediment.

c. The aqueous phase contaminant concentration is not solubility limited.

d. The gas phase is insignificant.

24. Equation 4 can be rearranged and written in terms of concentration as follows (see Appendix B):

$$q = K_d C \tag{5}$$

where

q = solid phase contaminant concentration, m_{i3}/m_3

m_{i3} = contaminant mass in solid phase

m_3 = sediment mass

K_d = distribution coefficient, L^3/m_3

C = aqueous phase contaminant concentration, m/L^3

25. In an open system such as that shown in Figure 1, the solid phase contaminant concentration, q, is not constant but decreases with time due to leaching by percolating water. If the rate of contaminant transfer across the sediment particle/pore water interface is rapid with respect to convective and dispersive transport in the pore water, the total contaminant mass is distributed between aqueous and solid phases according to Equation 5. Differentiating Equation 5 with respect to time yields

$$\frac{\partial q}{\partial t} = K_d \frac{\partial C}{\partial t} \tag{6}$$

26. In Appendix A, the source term, S, for equilibrium contaminant leaching is shown to be the partial derivative of q with respect to time. Substituting from Equation 6 for the partial derivative of q with respect to time yields

$$S = - \frac{\rho K_d}{\theta} \frac{\partial C}{\partial t} \tag{7}$$

where ρ is the bulk density (m_3/L^3) and θ is the volumetric water content. In the equilibrium approach, the source term is related to the change in aqueous phase contaminant concentration using a simple partitioning coefficient.

27. In general, K_d is not constant unless the ratio of solid and aqueous phase fugacities product is constant. If the phase reference fugacities are constant, K_d varies with changes in the chemical activity coefficient, γ. Chemical activity in the aqueous phase varies with ionic strength, pH, oxidation-reduction potential (Eh), and possibly other factors related to phase chemical potentials. The solid phase activity coefficients depend primarily on Eh and sediment geochemistry. Hence, K_d is a true constant

only if the fugacities of the solid and aqueous phases remain in constant ratio. With successive leaching, K_d may change depending on the stability of the chemical composition of each phase. Thus, factors that affect the constancy of distribution coefficients are important to the interpretation of leach tests.

28. Geochemical processes in the solid phase are relatively slow. For this reason, the solid phase fugacity is less variable than the aqueous phase fugacity. Karickhoff (1984) has reported evidence that the solid phase fugacity product is reasonably constant for hydrophobic organic chemicals. If this is true, K_d for hydrophobic organic chemicals will be primarily a function of the affinity of the compound for water. Karickhoff was able to correlate K_d to the water-octanol partition coefficient, K_{oc}. Significant economy could be realized through the use of such correlations in testing programs that require investigation of numerous chemicals. If the chemicals of interest can be classified into families of compounds with common partitioning characteristics, then information on one compound in a family may suffice to describe the entire family.

Adsorption isotherm equations

29. A brief description of adsorption-dominated equilibria is given in this section as a preface to the section on desorption-dominated equilibria. The adsorption process involves the association and preference of a sorbate for a solid substrate. For purposes here, adsorption will be viewed as a combination of elementary processes involved in the removal of materials from solution. While processes such as reversible and irreversible chemical reactions, physical entrapment, and precipitation are involved in adsorption, it is advantageous to consider these as a single process. However, on the theoretical level and for explaining observed phenomena, the various mechanisms should be recognized.

30. Adsorption isotherms have been used to define the equilibrium distribution of sorbate molecules between the solid phase and the aqueous phase (Weber 1972). Adsorption isotherms are determined by contacting varying quantities of sorbent with aliquots of fluid containing the sorbate. At equilibrium, each sample will have a different aqueous phase concentration and a different sorbed concentration. Consequently, a table of values may be generated for the mass of sorbate per mass of sorbent, q, versus the aqueous phase concentration, C. If the table values are plotted, a curve similar to

Figure 2 is usually obtained. It may be observed from the figure that the sorbent loading asymptotically approaches a limiting value as aqueous phase concentrations become large.

31. The Freundlich and Langmuir equations have been used to model the curve shown in Figure 2 (Weber 1972). The mathematical forms of the two equations differ as a result of differences in the kinetics that are modeled by the two equations. These differences are discussed in Appendix C. The Freundlich and Langmuir adsorption equations are presented as Equations 8 and 9, respectively.

$$q = KC^{1/n} \tag{8}$$

In Equation 8, K and $1/n$ are Freundlich coefficients, C is the mass concentration of a selected contaminant in the aqueous phase, and q is the contaminant mass concentration in the solid phase.

$$q = \frac{KQ_oC}{1 + KC} \tag{9}$$

In Equation 9, K is the Langmuir coefficient related to entropy and Q_o is the ultimate adsorbent capacity (monolayer) of the sorbent.

32. The Freundlich and Langmuir equations model the nonlinear region of the adsorption isotherm as well as the linear. The Langmuir is a particularly useful model of equilibrium-controlled organic pollutant removal by activated carbon adsorption because it takes into account the ultimate adsorption capacity of the sorbent. Each equation involves two empirical coefficients. Hence, several points on the isotherm are required in order to determine these coefficients. In the linear region of the adsorption isotherm where the adsorbed concentration is far below the adsorption capacity of the sorbent, a single distribution coefficient can be used to relate aqueous phase concentration to adsorbed phase concentration.

Desorption isotherms

33. Desorption isotherms are obtained by sequential batch leaching of contaminated sediment. When equilibrium is reached, the sorbed and aqueous phases are separated and analyzed. The sediment is then challenged by a new

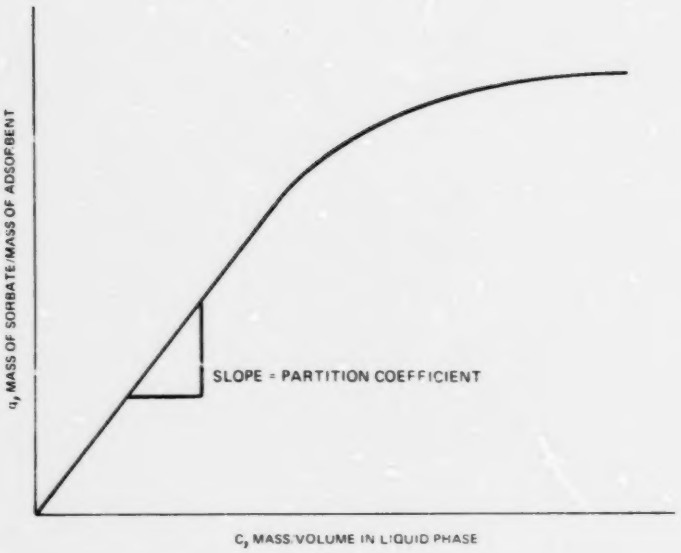

Figure 2. Adsorption equilibrium curve

(clean) aliquot of leaching medium until equilibrium is again reached. By repeating this procedure, a table of values can be generated for the mass of contaminant per mass of sediment, q, versus the aqueous phase concentration, C. If the table of values is plotted, a desorption-dominated isotherm will result. Like the adsorption isotherm, the desorption isotherm describes an equilibrium-controlled process.

34. If adsorption- and desorption-dominated processes take place under constant conditions, the desorption of a contaminant back into the aqueous phase should proceed down the curve provided by adsorption and follow it exactly. For this to take place, adsorption must be completely reversible, and identical sorption processes must take place going down the curve (desorption) as took place going up the curve (adsorption). Laboratory adsorption and subsequent desorption experiments by several investigators (Mustafa and Gamar 1972, DiToro and Horzempa 1982, Corwin and Farmer 1984) have shown that the sorption processes are not identical going up and coming down.

35. A hysteresis exists indicating that the relationship between sorbed and aqueous phases is different for adsorption-dominated and desorption-dominated processes. This means that a unique set of sorption coefficients that applies to both phenomena is unlikely. An idealized adsorption and

subsequent desorption isotherm for a sediment is shown in Figure 3. Since conditions for contaminant desorption in a CDF are probably quite different from those under which adsorption took place, the desorption or leaching behavior of the sediments cannot be predicted from knowledge of how the sediments became contaminated. Specific desorption isotherms are required. The two desorption lines shown in Figure 3 represent the reported dependency of desorption processes on the initial solid phase concentration (Corwin and Farmer 1984).

36. The desorption isotherms shown in Figure 3 can be extended to intercept the sorbent concentration axis. This intercept has been interpreted as irreversibly adsorbed material that is resistant to leaching (Crawford and Donigian 1973; Van Genuchten, Davidson, and Wierenga 1974; DiToro et al. 1982; Isaacson and Frink 1984). Other interpretations have been suggested (Curl and Keoleian 1984, Gschwend and Wu 1985). It is probably impossible to achieve thermodynamic equilibrium in batch desorption tests on dredged material. Geochemical processes initiated in shake tests may require months, even years, to reach completion. It is also possible that the "irreversibly" adsorbed fraction is leachable material contained in the internal sediment pores that is slowly released. In short-term batch tests designed to measure equilibrium distribution coefficients, this fraction, although leachable, could be interpreted as irreversibly adsorbed if the desorption rate for this fraction is low. Recently, Curl and Keoleian (1984) proposed an implicit adsorbate theory that accounts for both the hysteresis previously noted and an "apparent" irreversibly adsorbed fraction. Gschwend and Wu (1985) first explained the reported irreversibility as an experimental artifact caused by incomplete phase separation and later (Wu and Gschwend 1986) described an intraparticle diffusion model that accounts for the reported irreversibly adsorbed fraction as slowly diffusing material contained in intraparticle pores. There is no consensus in the literature regarding nonleachable and irreversibly adsorbed fractions or the relative significance of intraparticle pore phenomena on equilibrium status. Since this is an area that is not without dispute, additional work is needed before the differences between various theories can be resolved.

37. Just as the mathematical form of the adsorption-dominated isotherm equations depends on the kinetics used to model the process (see Appendix C), the mathematical form of desorption-dominated isotherm equations depends on

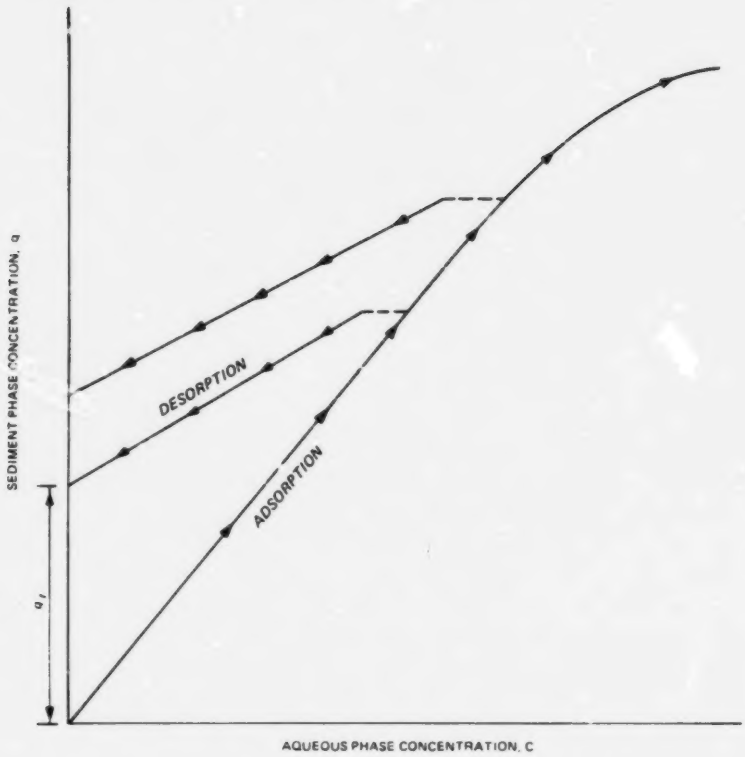

Figure 3. Adsorption/desorption plot

the kinetics used to model the process. Several desorption isotherm equations and, where appropriate, the kinetic equations from which they are derived are presented in Appendix D. Linear desorption isotherms can be modeled using Equation 10 below.

$$q = K_d C \tag{10}$$

where q and C are the equilibrium contaminant concentrations in the solid and aqueous phases, respectively, and K_d is the slope of the desorption isotherm. A term for a strongly or irreversibly absorbed fraction that does not leach, q_r, can be added as in Equation 11 below

$$q - q_r = K_d C \tag{11}$$

Equation 10 is identical to the result obtained in paragraph 23, and Equation 11 is only slightly more complicated. Each of these equations uses a

simple distribution coefficient to relate the aqueous phase contaminant concentration to the solid phase contaminant concentration. The simplicity of the equations provides significant computational advantages for modeling the source term. For linear, equilibrium-controlled desorption, the source term can be modeled with Equation 7. The same basic assumptions that apply to Equation 4 also apply to Equations 10 and 11. These assumptions are listed in paragraph 23.

36. Equations 10 and 11 model linear desorption processes. Since not all sorption processes are linear, it is informative to examine the conditions necessary for linearity. For the process to be linear, the experimentally determined coefficients, K_d and q_r, must be independent of C and q as well as solubility and adsorption limits. Equations 10 and 11 apply if the solid phase concentration, q, is much less than the ultimate adsorption capacity of the sediment and if the aqueous phase concentration is not solubility limited. If either phase is approaching its capacity to contain a contaminant(s) or if K_d is not independent of C and q, the isotherm will be nonlinear. Desorption-dominated isotherm equations that take into account phase capacity limits are described in Appendix D. A solid phase concentration dependency for distribution coefficients has been reported by several investigators (Houle and Long 1980; O'Connor and Connolly 1980; DiToro et al. 1982; Voice, Rice, and Weber 1983). With the aid of existing computer programs, nonlinear isotherms may also be used to model equilibrium-controlled desorption.

Isotherm summary

39. Isotherms are used to relate aqueous phase concentration to solid phase concentration whenever the sorption processes are equilibrium controlled. The equilibrium approach eliminates the need for additional rate equations and thereby provides a degree of mathematical simplicity. There is evidence that the desorption process for natural sediments is linear and that equilibrium modeling can be used (Jaffe and Ferrara 1983, Karickhoff 1984). Since there is, however, no consensus on the reversibility of sorption processes, additional work is needed to improve our basic understanding of contaminant leaching.

Nonequilibrium Processes

40. Adsorption/desorption processes that are removed from equilibrium have a potential toward change. For such cases, rate processes become important in describing the system's approach to equilibrium. The overall rate may be controlled by one of several processes. These include external diffusion through a film, internal diffusion within the interstices of the sediment solid phase, or reaction kinetics at the sediment/water interface (Weber 1972). Generally, rate processes are controlled by mass transfer rather than by the kinetics of chemical reactions. In many cases it can be assumed that reactions at a sorbent surface are instantaneous and the overall rate is controlled by mass transfer. However, because the processes involved in contaminant leaching from dredged material are not well understood at this point, both mass transfer and chemical reaction kinetics are discussed in this section on nonequilibrium processes.

Mass transfer

41. The overall rate of desorption may be controlled by mass transfer in one or more regions of the sediment/water system. These include the following: (a) nonsteady diffusion through a stagnant layer of water immediately adjacent to the external surface of each sediment particle; (b) intraparticle, aqueous-phase diffusion from desorption sites within the porous structure of the sediment particle to the exterior; (c) intraparticle, solid-phase diffusion to desorption sites; and (d) combined internal (solid and aqueous phases) diffusion and external diffusion (film) (Weber 1972).

42. Transfer in the various regions can be measured under circumstances for which transfer in the other regions has been eliminated or substantially suppressed. In some applications, mass transfer in all but one region can be logically eliminated. When this is done, mass transfer in one region is assumed to be rate controlling. Because of the elaborate nature of the testing required to completely define all aspects of the system, it is convenient to use a general resistance model to account for all the mass transfer processes that may be operative when one region cannot be assumed as rate controlling (Weber 1972, Thibodeaux 1979).

43. External (film) diffusion. Mass transport of a contaminant to or away from a sorbent surface is an important material transport mechanism in some systems (Bird, Stewart, and Lightfoot 1960; Treybal 1968; Weber 1972; Rao

et al. 1979). The film theory of interphase transport assumes that the rate of desorption is controlled entirely by the rate of contaminant diffusion (mass transfer) across a laminar film that separates the sediment surface and the bulk of the aqueous phase. Figure 4 describes the general model of external diffusive transfer that will be used here. This visualization shows a concentration boundary layer (thin film) extending from the sediment/water interface to the edge of a hypothetical film. The contaminant concentration falls from C_{i1} at the sediment/water interface to C_{i2} in the bulk of the aqueous phase. This is perceived as the direction of contaminant flux after dredging. If the fluid flow across the sediment surface is laminar, the thickness of the film is governed by molecular diffusion. If the flow is turbulent, the thickness is governed by eddy diffusion.

44. For diffusion through a stagnant film, the diffusion equation is (Bird, Stewart, and Lightfoot 1960)

$$\frac{\partial C_i}{\partial t} = D_i \frac{\partial^2 C_i}{\partial y^2} \tag{12}$$

where

$\frac{\partial C_i}{\partial t}$ = time rate of change in the i^{th} contaminant concentration, M/vt

D_i = diffusivity of the i^{th} contaminant in the aqueous phase, L^2/t

$\frac{\partial C_i}{\partial y}$ = change in the i^{th} contaminant concentration with respect to y, M/vt

C_i = mass concentration of i^{th} contaminant, M/t

y = space dimension representing distance away from the sediment/water interface as defined in Figure 4, L

The general form of this equation is used to describe a wide variety of mass transfer operations. The uppercase D is sometimes written as script E so as to indicate molecular diffusion and/or eddy diffusion. Outside theoretical discussions, distinction is usually not made between molecular and eddy diffusion in film-limited transfer. The diffusion coefficient can also be described in other ways and by other variables (Treybal 1968, Weber 1972, Thibodeaux 1979).

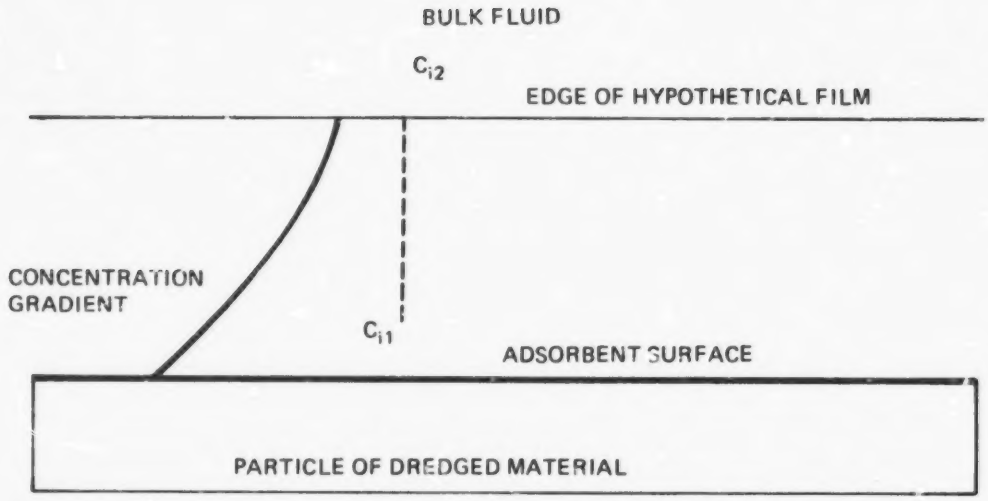

Figure 4. Mass transfer model for external diffusion

45. In many problems the integrated form of Fick's law is used, and a K , K_a , K_{La} , or othe substitute is used for the Fickian script D. A very important assumption is implicit in such formulations, that D_i is constant. Treybal (1968) recognizes K as a local mass transfer coefficient that is not necessarily constant. Even with this deficiency, this form is widely used for many applications (Treybal 1968, Thibodeaux 1979). For steady-state diffusion of contaminant i through a thin film, $\partial C/\partial t = 0$. When steady-state conditions exist, Equation 12 can be integrated to yield the integrated form of Fick's Law

$$N = \frac{D}{y_f} \frac{A}{V} (C_e - C) \tag{13}$$

where

N = contaminant flux at the edge of the hypothetical film, m/L^2t

y_f = effective film thickness, L

$\frac{A}{V}$ = area of transfer across fluid film per bed volume, L^{-1}

C_e = aqueous phase equilibrium contaminant concentration at the sediment/water interface, m/L^3

C = bulk aqueous phase contaminant concentration beyond the edge of the film, m/L^3

46. The aqueous phase equilibrium contaminant concentration at the sediment/water interface is the same quantity as defined in Equations 10 and 11. The effective film thickness, y_f, is a quantity not easily measured. To get around this problem, the contaminant flux can be described in terms of a mass transfer coefficient, K_f, as follows:

$$N = K_f \frac{A}{V} (C_e - C) \tag{14}$$

where $K_f = D/y_f$ = film mass transfer coefficient, L/t .

47. The film model requires that the contaminant concentration immediately adjacent to the boundary surface of the sediment particle is in equilibrium with the solid phase concentration at the sediment/water interface. It is also evident that the rate of steady-state diffusive mass transfer through the film is directly proportional to the driving force, which in this case is $C_e - C$. Thus, the contaminant flux, N , varies with the difference $C_e - C$. It is informative to note that K_f really is not a simple constant but rather a combination of terms involving the diffusion coefficient and the film thickness. These parameters, in turn, are dependent on the physical-chemical properties of the contaminant and the aqueous phase, and on the hydrodynamics of the flow regime. The dependency of K_f on hydrodynamics and physical properties has been used to provide a means for calculating a film mass transfer coefficient (Chu, Kalil, and Wetteroth 1953).

48. The overall, film mass transfer coefficient, K_f , can be correlated to the dimensionless mass transfer coefficient, J_D , which in turn is correlated to the Sherwood number (N_{sh}), the Reynolds number (N_{Re}), and the Schmidt number (N_{Sc}) (Treybal 1968, Thibodeaux 1979).

$$J_D = \frac{N_{sh}}{N_{Re}} N_{Sc}^{1/3} \tag{15}$$

and

$$K_f = N_{sh} \frac{D}{y_f} \tag{16}$$

where

$$N_{sh} = \frac{K_f d_p}{D}$$

d_p = mean particle diameter, L

D = molecular diffusivity of the contaminant, L^2/t

$$N_{Re} = \frac{v d_p}{\nu}$$

v = mean velocity in the bulk of the fluid, L/t

ν = kinematic viscosity of the fluid, L^2/t

$$N_{Sc} = \frac{\nu}{D}$$

49. Substituting these definitions into Equation 14 yields

$$K_f = \frac{J_D D^{2/3}}{\nu^{2/3}} \tag{17}$$

50. Several investigators have conducted intensive studies to determine empirical equations relating J_D to the Reynolds number. Chu, Kalil, and Wetteroth (1953) relate these parameters as follows:

$$J_D = 5.7 * N_{Re}^{-0.78} \quad \text{for } 30 > N_{Re}$$

$$J_D = 1.77 * N_{Re}^{-0.44} \quad \text{for } 1{,}000 > N_{Re}$$

51. The above relationships can be used to estimate a film mass transfer coefficient, K_f, based on the fluid velocity in the bulk aqueous phase, the aqueous phase viscosity and density, molecular diffusivity of the contaminant, and the mean particle diameter. If Equation 14 is rearranged to yield

$$C = C_e - \frac{N}{K_f \frac{A}{V}} \tag{18}$$

then

$$C = C_e \tag{19}$$

when the effective film thickness approaches zero. As the effective film thickness increases, the film model predicts a decline in C that is related to the hydraulics of the system.

52. The shaking action generally employed in laboratory batch sorption tests tends to reduce the boundary layer thickness. In this case, as indicated in Equation 19, the bulk aqueous concentration, C, approaches the equilibrium concentration, C_e, at the sediment surface. The system hydraulics in a CDF are quite different. The fluid velocity in the CDF may not be high enough to prevent the development of a significant boundary layer. Since the fluid velocity at the particle surface is necessarily zero, a laminar boundary layer will develop in which a contaminant concentration gradient will exist as shown in Figure 4. In the treatment given above, the boundary layer was treated as a stagnant film. This is a reasonable approximation when the fluid velocity outside the film is very low, as in a CDF.

53. The above considerations imply that the equilibrium concentration, C_e, measured in laboratory batch sorption tests will probably not be the actual bulk aqueous phase concentration, C, in a CDF. Due to the presence of a boundary layer around each sediment particle, the bulk aqueous phase concentration will be slightly less depending primarily on the system hydraulics and the diffusivity of the contaminant in the aqueous phase. The source term modified for film-controlled transfer of contaminant to the aqueous phase is given by

$$S = -\frac{\rho}{\theta}\frac{\partial q}{\partial t} = -K_f \frac{A}{V}(C_e - C) \tag{20}$$

where $\frac{\rho}{\theta}\frac{\partial q}{\partial t}$ is the source term defined in Equation 2.

54. Internal diffusion. Internal diffusion within the sediment particles controls the transfer of contaminants from the interior of the particle to the particle/water interface. These processes are usually very slow in comparison

to other processes, and in many circumstances they can be ignored. If they are ignored, the implied assumption is that contaminants in the internal pores are not leachable.

55. Although internal contaminant mass transfer may occur primarily by aqueous phase diffusion in intraparticle pores, other mass transport processes such as solid phase diffusion to the pore walls and solid phase diffusion along the pore walls may also occur. It is advantageous to consider intraparticle mass transport as a single, diffusion process. The one-dimensional equation for Fickian diffusion through the interstices of a porous, isotropic solid is (Crank 1956)

$$\frac{\partial q_i}{\partial t} = D_e \frac{\partial^2 q_i}{\partial x^2} \tag{21}$$

where

q_i = solid phase i^{th} contaminant concentration, m_c/m_s
m_c = mass of contaminant
m_s = mass of solid
D_e = effective diffusion coefficient, L^2/t
x = space dimension inside the sediment particle, L

56. The diffusion coefficient is referred to as an effective coefficient because it is a lumped parameter that accounts for aqueous phase diffusion in intraparticle pores and solid phase diffusion within the particle. It is unique to each contaminant and each type of particle. Several investigators (Godbee and Joy 1974; Moore, Godbee, and Kibbey 1976; Godbee et al. 1980) have used Equation 21 to model internal diffusion-controlled leaching of radionuclides from solidified nuclear waste. First, Lowenbach (1978) and, more recently, Cote (1986) have proposed modeling the leaching of solidified industrial waste (nonnuclear) using Equation 21.

57. For intraparticle diffusion as the rate-controlling leaching mechanism, Equation 21 is the governing equation for transport of contaminant from the solid phase to the aqueous phase. If the particles are homogeneous, if the contaminant is initially uniformly distributed throughout the particle, and if the particle surface concentration is always zero (contaminant is

leached as soon as it arrives), the appearance of contaminant in the aqueous phase for a semi-infinite particle is given by Equation 22 (Godbee et al. 1980).

$$\frac{\sum a}{A} = 2\left(\frac{D_e}{\pi}\right)^{1/2} t^{1/2} \frac{S}{V} \tag{22}$$

where

$\sum a$ = total contaminant mass appearing in the aqueous phase, m_c

A = initial amount of contaminant internally contained in the sediment particles, m_c

D_e = effective diffusivity solid phase, L^2/t

t = time

$\frac{S}{V}$ = specific surface area, L^{-1}

58. In Equation 22, the cumulative fraction of contaminant appearing in the aqueous phase is directly proportional to time to the one-half power, where the proportionality constant is given by

$$2B = 2\left(\frac{S}{V}\right)\left(\frac{D_e}{\pi}\right)^{1/2} \tag{23}$$

59. Equation 22 can be written in terms of the solid phase contaminant concentration and B as follows:

$$\frac{q_o - q}{q_o} = 2Bt^{1/2} \tag{24}$$

where q_o is the initial concentration of contaminant internally contained in the sediment particles. For the case of contaminant leaching controlled by intraparticle diffusion, the source term is

$$S = -\frac{\rho}{\theta}\frac{\partial q}{\partial t} = -\frac{\rho}{\theta} Bq_o t^{-1/2} \tag{25}$$

where $\frac{\rho}{\theta}\frac{\partial q}{\partial t}$ is the source term as derived in Appendix A. The above equation applies if the particle phase concentration at the surface is zero. This implies that all the readily desorbable contaminant has been leached and only that contaminant residing beneath the surface is left. Internal diffusion-controlled leaching probably does not become important until all the readily desorbable contaminant on the particle surface has been depleted.

60. Intraparticle transport can also be modeled using a "lumped parameter" model. A lumped parameter source term is similar to the source term described above for solid phase diffusion. The lumped parameter source term is given by

$$S = -kp\left(\langle q \rangle - q_e\right)\left(\frac{S}{V}\right)\left(\frac{\rho}{\theta}\right) \tag{26}$$

where

kp = in-particle effective mass transfer coefficient, L/t

$\langle q \rangle$ = average contaminant concentration with the particle, m_c/m_s

q_e = the surface concentration in equilibrium with the bulk liquid, m_c/m_s

In this model the source strength is proportional to the difference between the average contaminant concentration within the particle and the surface concentration in equilibrium with the bulk liquid. Unlike the solid phase diffusion model, an infinite contaminant source is not assumed.

Chemical kinetics

61. Mass transfer considerations are important in leaching studies. Chemical kinetics may also be important under certain conditions. In this section, the rate limiting step is assumed to be chemical reactions occurring on the particle surface; i.e., transfer of material between phases is limited by chemical kinetics.

62. The geochemical reactions occurring within dredged material are diagenetic; i.e., they may be abiotic or biogenic. Biogenic reactions are largely responsible for the removal of oxygen, production of carbon dioxide, sulfate and nitrate reduction, and the production of ammonia, methane, and hydrogen sulfide. Abiotic reactions include dissolution of minerals, recrystallization of minerals, precipitation of low-solubility salts, and

crystalline substitution. When the reaction rates are such that equilibrium is attained very slowly (if ever), the kinetics of the reactions are rate controlling. The following discussion is applicable to kinetically controlled sorption processes as well as the geochemical processes involved in the dissolution of sparingly soluble contaminants from the surface of the sediment particles. Biological processes may well be important, but they are beyond the scope of the present discussion.

63. Again, the model shown in Figure 4 will be used. Component A is attached to the sediment particle and is in equilibrium with its surroundings. When clean water is brought into contact with the sediment, kinetically controlled desorption and/or dissolution of sparingly soluble compounds occurs until equilibrium is reached. It is assumed that diffusion of contaminant away from the surface is not rate controlling.

64. Irreversible reactions. The simplest types of reactions to describe are classified as irreversible reactions. An example is as follows:

$$A \xrightarrow{K} B$$

In such a reaction, component A is converted to B, but no conversion of B back to A occurs. A generalized first-order reaction rate can be written as

$$\frac{dA}{dt} = -KA \tag{27}$$

where dA/dt is the change in concentration of A with time, K is the reaction rate constant, and A is the concentration of A remaining at time t. The negative sign arises because A is disappearing. For a two-phase (sediment-water) system undergoing desorption, the analogous equation is

$$\frac{dq}{dt} = -Kq \tag{28}$$

In this case the source term is given by

$$S = -\frac{\rho}{\theta}\frac{\partial q}{\partial t} = \frac{\rho}{\theta} Kq \qquad (29)$$

65. In order to use Equation 29, the initial concentration of contaminant in the solid phase must be known, and K must be evaluated using Equation 28. In order to determine K, it is necessary to collect rate data of q versus t. A plot of first-order, irreversible data would resemble the curve shown in Figure 5.

66. The dissolution rate for a sparingly soluble contaminant can be described by an equation of the form (Lowenbach 1978)

$$\frac{dA}{dt} = ks(A_s - A)^n \qquad n > 0 \qquad (30)$$

where

A = contaminant concentration at time t

k = dissolution rate constant

s = available surface area

A_s = saturation concentration of A

n = empirical coefficient

This equation describes a system in which the rate of desorption is dependent on the solubility of A. When applied to a sediment-water system, this equation can be written as

$$\frac{dq}{dt} = -k(C_s - C)^n \qquad n > 0 \qquad (31)$$

where $k = ks$ and C_s is the saturation concentration of the contaminant of interest. In this case, the source term is given by

$$S = -\frac{\rho}{\theta}\frac{\partial q}{\partial t} = \frac{\rho}{\theta} k(C_s - C)^n \qquad n > 0 \qquad (32)$$

Values of k and n can be determined from laboratory data using Equation 31, provided C_s and the initial concentration of contaminant in the solid phase are known.

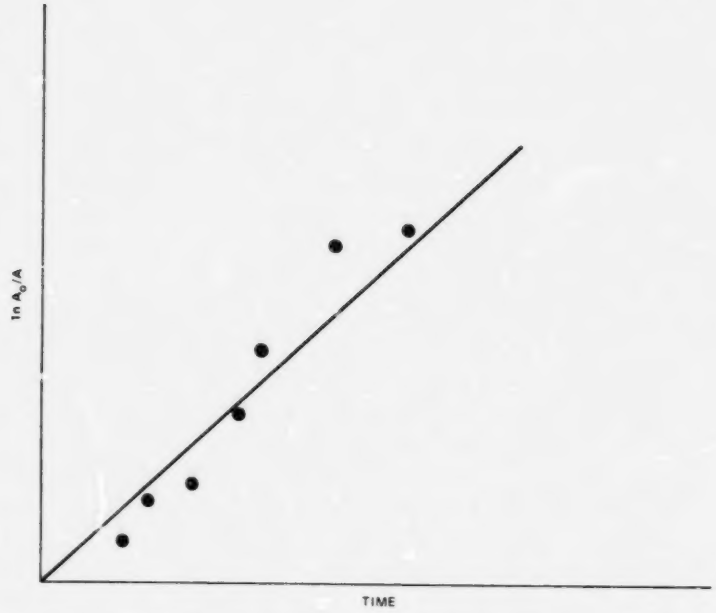

Figure 5. Graphical determination of first-order reaction kinetics

67. Reversible reactions. The second type of first-order kinetics is the reversible reaction

$$A \underset{K_R}{\overset{K_F}{\rightleftharpoons}} B \tag{33}$$

This reaction shows that as B is being generated, a reverse reaction is also going on that depletes B . If the rate of both the forward and reverse reactions can be described by first-order kinetics, the net rate of disappearance of A may be represented as

$$\frac{dA}{dt} = -K_F A + K_R B \tag{34}$$

68. When applied to a sediment-water system, the analogous equation is

$$\frac{dq}{dt} = -K_F q + K_R C \tag{35}$$

In this case, contaminant is appearing in the aqueous phase as C at a rate equivalent to $K_F q$. Similarly contaminant is reappearing in the solid phase as q at a rate equivalent to $K_R C$. The source term in this case is given by

$$S = - \frac{\rho}{\theta} \frac{\partial q}{\partial t} = - \frac{\rho}{\theta} -K_F q + K_R C \tag{36}$$

69. If the shift away from equilibrium is slight, the ratio of solid and aqueous phase contaminant concentrations will approach the ratio defined by the distribution coefficient, K_d , discussed in paragraph 37. If the shift is large enough, the aqueous phase contaminant concentration will be lower than that defined by the distribution coefficient. The relationship between the reversible reaction mechanism postulated in Equation 33 and the equilibrium distribution coefficient K_d is defined by

$$K_d = \frac{K_R}{K_F} \tag{37}$$

70. Values of $K_d < 1$ imply that the reaction is shifted to the right; that is, desorption dominates. Values of $K_d > 1$ imply an equilibrium position shifted to the left; that is, adsorption dominates. This is generally the case for hydrophobic organic compounds (Jaffe and Ferrara 1983).

Nonequilibrium summary

71. The available literature suggests that sorption processes in natural systems are not kinetically controlled. An instantaneous equilibrium approach is the more common assumption. However, for some contaminants and some sediments, this may not be appropriate. Thus, equilibrium versus kinetic approaches for desorption will have to be evaluated on a case-by-case basis.

72. In nonequilibrium situations, intraparticle pore phenomena are more likely to be rate controlling than chemical reaction kinetics for hydrophobic organics. If intraparticle mass transfer is involved, the source term will be proportional to time to the negative one-half power. If first-order reactions at the sediment/water interface are involved that are not solubility limited, the source is proportional to the contaminant concentration in the sediment phase. If reactions are involved that are solubility limited, the source term

will be proportional to the difference between the solubility limit and the aqueous phase concentration, this difference raised to some power greater than zero. As a first approximation, organic contaminants that are not equilibrium controlled can be assumed to be controlled by intraparticle diffusion. Inorganic contaminants that are known to be sparingly soluble will probably be controlled by solubility-limited reaction kinetics. A summary of the source equations that have been described in this section and in the previous section on equilibrium-controlled desorption is provided as Table 1.

Table 1

Summary of Source Term Formulations

Model Adsorption	Basic Equation	Resulting Source Term	Comments and Location in Text
Desorption - equilibrium			
Equilibrium model	$q = K_d C$	$S = -\frac{\rho}{\theta}\frac{\partial q}{\partial t} = -\frac{\rho K_d}{\theta}\frac{\partial C}{\partial t}$	Assumes no irreversibly adsorbed fraction. Numerical values of K_d not generally equal to those for adsorption; paragraphs 33-38.
Equilibrium model	$q = q_r + K_d C$	$S = -\frac{\rho}{\theta}\frac{\partial q}{\partial t} = -\frac{\rho K_d}{\theta}\frac{\partial C}{\partial t}$	Variable q_r is an irreversibly adsorbed contaminant fraction; paragraphs 33-38.
Desorption - non-equilibrium - physical			
Film effects model, internal or external	$\frac{dc}{dt} = \frac{Ddc^2}{dy^2}$	$S = -K_f(C_e - c)\frac{A}{V}$	Solute transfer governed by transport across a stagnant film surrounding sediment particle; equilibrium relationship required at liquid-particle interface; paragraphs 40-47.
Semi-infinite diffusion model - solid phase	$\frac{dq}{dt} = \frac{D_e dq^2}{dx^2}$	$S = -\frac{\rho}{\theta} Bq_o t^{-1/2}$	Solute transfer governed by solid phase diffusion from semi-infinite surface; solute concentration at particle surface assumed equal to 0; paragraphs 54-59.
Lumped parameter, particle model		$S = -kp\left(\langle q\rangle - q_e\right)\left(\frac{A}{V}\right)\left(\frac{\rho}{\theta}\right)$	Variable K_p determined from laboratory studies, assumption of infinite source not required. Equilibrium relationship at particle-liquid interface required.
Desorption - non-equilibrium - chemical			
First-order, irreversible reaction	$\frac{dq}{dt} = -Kq$	$S = \frac{\rho}{\theta} Kq$	Source strength not limited by solubility considerations; paragraph 64. Liquid-particle equilibrium relationship required.
n^{th}-order kinetics, solubility limited	$\frac{dq}{dt} = -k(C_s - C)^n \quad n > 0$	$S = \left(\frac{\rho}{\theta}\right)k(C_s - C)^n \quad n > 0$	Source strength dependent on solubility of contaminant. Variable C_s required; k and n determined by laboratory analyses; paragraph 66.
First-order, reversible reaction	$\frac{dq}{dt} = -K_F q + K_R C$	$S = -\frac{\rho}{\theta}(-K_F q + K_R C)$	Variables K_F and K_R must be determined by laboratory analyses; paragraph 67.

PART IV: PREDICTION OF CONTAMINANT LEACHING FROM DREDGED MATERIAL

73. The first step in developing a predictive protocol is to single out the important processes involved and to describe these processes mathematically. This was done in PART III of this report. Sometimes, given the present state of knowledge, the mathematical descriptions needed cannot be derived entirely from theoretical arguments. In such cases, it is necessary to use available experimental data and existing empirical correlations. The second step is to introduce simplifying assumptions that make the mathematics tractable. These assumptions stem from physical arguments. Sometimes, simplifications are needed because without them the equations involved cannot be solved. Sometimes, simplifying arguments arise out of an examination of the practical aspects of the theory and are not necessarily related to a need to simplify. In its final form, a predictive protocol is a compromise involving the complexity of the problem, the investigator's understanding of the important processes, and the limits of mathematics (Stanislav 1982).

74. In the following discussion, the second step in the development of a predictive protocol for contaminant leaching from dredged material in CDF's is addressed. Two interrelated aspects of protocol development and application are discussed. First, simplifications related to the principles of transport theory are introduced and discussed. Then, factors that affect the environmental chemistry of dredged material are discussed. These factors significantly affect all the input parameters to the mass transport equation.

Application of Transport Theory

75. The principles discussed in PART III have been utilized in a variety of problems, especially chemical engineering problems. Recently, these principles have been applied to environmental problems (Thibodeaux 1979). One hindrance to the application of these principles to contaminant transport is the complexity of the environment. Without simplifying assumptions, certain problems may not be solvable. Or if they can be solved, the specific problem of interest may not justify the resources required to arrive at a solution. In the section that follows, the utility and justification of selected simplifying assumptions related to transport theory are presented.

76. Figure 6 presents a visual model for a dredged material particle. The particle contains a contaminant attached to the surface. It will be noted that only a small portion of the surface is covered. It has been observed that the actual quantity of sorbed contaminant is typically one to many orders of magnitude less than the adsorption capacity (O'Connor and Connolly 1980). The diagram also shows a limited pore structure. This aspect may or may not be important in dredged material studies. The figure also shows a film surrounding the particle. This film may be thought of in terms of a resistance to mass transfer. Three potential rate-limiting steps may be described as follows:

a. Intraparticle diffusion of contaminant from inside the particle to the particle surface, either aqueous or solid phase.

b. Surface desorption reaction and solubilization.

c. Diffusion through a boundary layer film.

77. For purposes of the discussion here, the simplifying assumption is made that in a two-phase system, items a, b, and c represent all the important leaching processes for dredged material. Using this assumption, the source term is generally defined in terms of the process assumed to govern (limit) contaminant transport, which in turn depends on the fundamental properties of the desorption system. This is expressed as follows:

$$\text{Source strength} = \begin{matrix}\text{Equilibrium processes} \\ \underline{\text{or}}\ \text{Film diffusion}\ \underline{\text{or}} \\ \text{Intraparticle diffusion}\end{matrix}$$

Further definition of the source term for dredged material will require laboratory analyses and data interpretation.

78. At this point, sufficient data are not available to reduce the above expression to a single process. For example, there is virtually no information available on the relative significance of film effects for dredged material. Hence, film effects cannot be assumed to be negligible. The literature on desorption processes indicates that it is unclear whether sorption is entirely or only partially reversible (Voice, Rice, and Weber 1983; Curl and Keoleian 1984). Although equilibrium-controlled desorption has been assumed or stated to be the case, very little rate data is available.

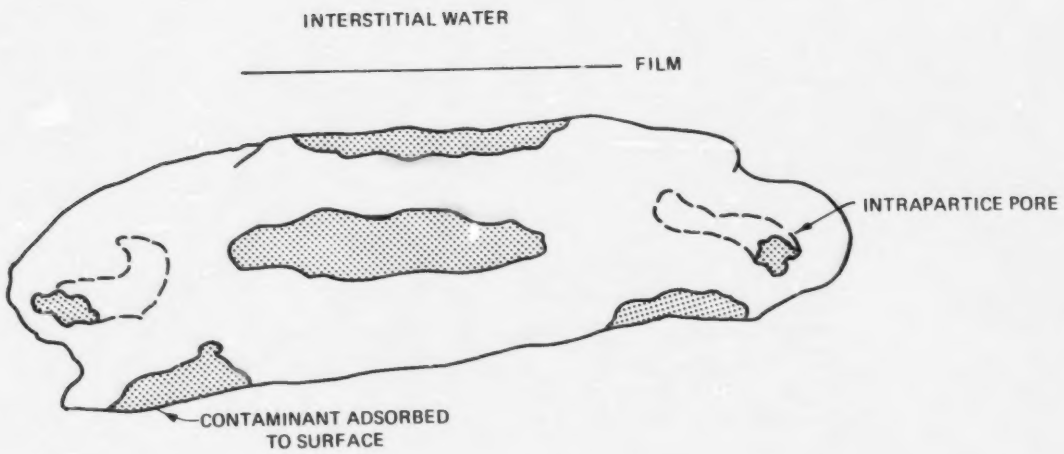

Figure 6. Visual model of a dredged material particle

79. A reasonable strategy to follow is to select the simplest process, equilibrium-controlled desorption, for evaluation in an experimental program. If analysis of the data shows that equilibrium-controlled desorption satisfactorily describes the source term, there is no need to consider the other processes. Regardless of the formulation, the coefficients for the source term are contaminant specific. Further, they vary with the leaching conditions under which contaminant transfer takes place. Since the coefficients used as input to the mass transport equation depend on various physical-chemical factors that influence contaminant mobility, it is important that laboratory test procedures represent realistic field conditions.

Factors Influencing Contaminant Mobility in Dredged Material

80. Contaminant mobilization in dredged sediments has been difficult to describe because of the complex nature of dredged material (Brannon et al. 1976) and the site-specific interactions that different contaminants exhibit with sediments (O'Connor and Connolly 1980). Contaminants associated with sediments range from those that are highly mobile to those that are highly immobile. There is evidence that in most sedimentary environments, only a small portion of the chemical constituent associated with a sediment is in a highly mobile form (Fulk, Gruber, and Wullschleger 1975; Brannon et al. 1976; DiToro et al. 1982). For example, a significant fraction of the total amount

of many metals is part of the crystalline lattice of sediment minerals, and probably should not be considered as mobile contaminants (Brannon et al. 1976; Brannon, Plumb, and Smith 1978). With regard to organic contaminants, there have been conflicting reports on the presence of an irreversibly adsorbed fraction that does not leach (Crawford and Donigian 1972, DiToro et al. 1982, Corwin and Farmer 1984, Curl and Keoleian 1984, Isaacson and Frink 1984).

81. Contaminant mobility was interpreted in terms of interphase fugacities in paragraph 23. Phase fugacities determine whether or not interphase contaminant transfer is thermodynamically feasible (Mackay 1979). The chemical thermodynamic properties of a system are highly dependent on the physical-chemical properties of the system. Many factors have been identified as critical in influencing the mobility of contaminants in dredged materials. These include, but are not necessarily limited to, redox potential (Gambrell et al. 1977, Mang et al. 1978), dissolved oxygen concentration, time of contact, solid-liquid ratio, and pH (Lee and Plumb 1974). These and other important factors which regulate contaminant release from dredged materials, and therefore impact the source term in the mass transport equation, are discussed below.

Redox potential

82. In sediments or in CDF's with ponded water, oxygen enters the sediment by molecular diffusion (Ponnamperuma 1972). This results in a sediment that has a low redox potential, is virtually devoid of dissolved oxygen, and contains reduced components such as NH_4^+-N, H_2S, Mn^{+2}, Fe^{+2}, and CH_4, plus refractory organic matter. The sediment may or may not have a thin surface oxidized layer, depending on the aeration status of the overlying water (Ponnamperuma 1972) and the oxygen demand of the sediment (Patrick and Mikkelsen 1971). The underlying bulk of the sediment generally exhibits a low redox potential (<-150 mV) (Brannon et al. 1976).

83. When a dredged sediment is placed in a CDF, exposure to air during the dredging and disposal results in short-term perturbations of the sediment redox regime. Due to the high oxygen demand of most sediments, the initial stage of leaching is under anaerobic conditions. If the CDF is not managed to remove ponded water, the sediment in the CDF will remain anaerobic. If the site is in an area where evaporation exceeds precipitation or if the site is managed to remove ponded water, the material will gradually transition from an anaerobic to an aerobic environment. The timing of this transition is site

specific and depends on site management practices. The initial stages of oxidation are characterized by drying and cracking of the sediment surface in the CDF and development of a crust over the site. Over the projected life of a site, leaching can occur under conditions ranging from strongly anaerobic to mildly aerobic or under a combination of the two (i.e., oxidized sediment overlying anaerobic sediment).

84. The redox potential and oxidation status of the sediment can greatly affect the aqueous solubility of contaminants. For example, zinc and cadmium release from dredged materials is highest under oxidizing conditions (Patrick, Gambrell, and Khalid 1977). The impact of redox potential on metal solubility and release mechanisms is also discussed by Gotoh and Patrick (1972); Gambrell, Khalid, and Patrick (1976); and Khalid, Gambrell, and Patrick (1977). Because redox potential significantly affects the mobility of metal contaminants, any series of tests developed to provide input into the source term of the mass transport equation must be able to provide coefficients under either anaerobic or aerobic conditions or a combination of the two.

Dredged material pH

85. In anaerobic soils and sediments, the pH is buffered near neutrality by the action of substances produced as a result of reduction reactions (Patrick and Mikkelsen 1971, Ponnamperuma 1972). The most likely compounds responsible for this buffering action are iron and manganese compounds in the form of hydroxides and carbonates, and carbonic acid (Patrick and Mikkelsen 1971). When a sediment becomes oxidized, the anaerobic processes that buffer pH become inoperative. This can result in strong acidification (pH 4.0 or less) and enhanced release of metal contaminants (Brannon, Plumb, and Smith 1978; Brannon 1984) by increasing their solubilities. This is most pronounced for trace metals associated with sediments. Zinc, cadmium, and lead, for example, are much more soluble under acidic conditions than under neutral to alkaline pH conditions (Patrick, Gambrell, and Khalid 1977; Trefry and Metz 1984).

86. It is evident that pH changes in dredged material following disposal can result in changes in contaminant mobility. The changes in sediment pH that occur under aerobic conditions are highly site specific, with the majority of sediments tested showing no severe drops in pH (Brannon 1984). The drop in pH is not instantaneous and may require a number of months to manifest itself. Laboratory tests designed to indicate contaminant mobility in dredged

material must therefore be designed to allow the sediment to impose its own pH regime on the leachate. This will require that sediments be allowed to oxidize naturally and reach their own pH level prior to testing.

Solids-to-liquid ratio

87. For a wide range of contaminants, distribution coefficients have been shown to be inversely related to the solids-to-liquid ratio (DiToro et al. 1982; O'Connor and Connolly 1982; Voice, Rice, and Weber 1983). This effect was found to be most pronounced for compounds such as DDT and cobalt that exhibit high partition coefficients. Solids concentration-dependent partitioning appears to be a function of the solids, not the compound (O'Connor and Connolly 1980). It has been suggested that particle-particle interaction may be responsible for such solids-dependent partitioning (DiToro et al. 1982). The dependency of distribution coefficients on solid/liquid ratios has also been explained as an experimental artifact related to incomplete phase separations (Gschwend and Wu 1985). Due to inadequate phase separation, nonsettling and nonfilterable microparticles are included in the chemical analysis of the aqueous phase. This increases the apparent aqueous phase concentration (reduces the distribution coefficient). Since the effect is exaggerated at high solid/liquid ratios, the distribution coefficient appears to be inversely related to the solid/liquid ratio. It has been postulated that at high solid/liquid ratics (500,000 mg/ℓ, an approximate average value for bed sediments), a limiting value of the distribution coefficient may be reached (O'Connor and Connolly 1980).

88. Theoretical considerations based on the fugacity concept predict that distribution coefficients will vary with the environmental conditions, including solid/liquid ratios used in a batch sorption test. The fugacity basis for defining a partitioning coefficient (see Appendix B) is as follows:

$$K_p = \frac{fo_3 \gamma_3 X_3}{fo_2 \gamma_2 X_2} \tag{38}$$

By assuming that

$$\frac{fo_3 \gamma_3}{fo_2 \gamma_2} = \text{Constant}$$

The partition coefficient can be written as

$$K_d = \frac{\text{Solid phase concentration}}{\text{Aqueous phase concentration}}$$

89. Obviously, if the reference phase fugacities or the chemical activities vary, K_d will probably not be a constant. The solid phase reference fugacity product ($fo_3\gamma_3$) is not highly variable (Karickhoff 1984). The aqueous phase fugacity product ($fo_2\gamma_2$), however, will vary depending on pH, oxidation-reduction potential, temperature, ionic strength, and to a lesser degree, pressure (Mackay 1979, Thibodeaux 1979). When a sediment is contacted with clean water in a desorption-dominated batch test, the sediment will, by imposing its particular chemistry on the aqueous phase, determine the aqueous phase pH, ionic strength, chemical activity and, to some extent, oxidation-reduction potential. At each solid/liquid ratio, the aqueous phase fugacity is redefined. Hence, partition coefficients vary with the solid/liquid ratio used in a batch sorption test to the extent that the aqueous phase chemistry varies with liquid/solid ratio.

90. An implicit-adsorbate model (Curl and Keoleian 1984) has been proposed that explains the dependency of the distribution coefficient on the solid/liquid ratio in a fashion conceptually analogous to the use of the fugacity concept. According to the implicit-adsorbate model, during batch desorption experiments the sediment releases the adsorbate, component A, that is under study. Another adsorbate, component B, is also released. The release of B uncovers binding sites for A. The number of sorption sites available for A will be higher when most of B is in the aqueous phase. If B readily desorbs, the apparent partition coefficient at a low solid/liquid ratio for component A can be higher than when a high solid/liquid ratio is used because in the latter the mass of water available for solution of B is less.

91. The constancy of sediment/water partition coefficients is an area of concern and could have a bearing on sediment/water ratios used in batch tests for dredged material. Coefficients developed at one solid/liquid ratio may not be appropriate at another ratio. Laboratory tests must therefore be designed to provide batch sorption coefficients consistent with those that exist at the solid/liquid ratios found in the field situation.

Other factors

92. In developing the dredged material elutriate test, Lee et al. (1975) demonstrated that dissolved oxygen concentration during the tests was critical. This has a number of ramifications for testing conducted under anaerobic conditions. Failure to preserve the anaerobic integrity of sediments during sampling, handling, and storage will result in alteration of contaminant distribution among the various sediment phases (Chen et al. 1976). This change in phase can render the contaminant either more or less mobile, as for example, the precipitation of ferrous iron when anaerobic sediments are exposed to air (Brannon et al. 1976). After sampling, a sediment should be stored under conditions that minimize microbial activity. It is also extremely important to exclude air during all steps of testing if anaerobic conditions are to be maintained (Brannon et al. 1976).

93. In regard to other considerations, separation of solid and liquid phases is most conveniently done by centrifugation followed by filtration (Brannon et al. 1976). Direct filtration without centrifugation has been shown to be unacceptable due to greatly increased processing times and expense (Lee et al. 1975).

PART V: LABORATORY PROCEDURES FOR INVESTIGATING CONTAMINANT MOBILITY IN DREDGED MATERIAL

Current Test Procedures

94. Two principal laboratory testing procedures are used to investigate the leachability of wastes (Perket and Webster 1981, Conway and Gulledge 1983). These are the column testing and batch testing procedures. In this part, the recommended laboratory testing procedures and technical rationale needed to accomplish the objectives stated in the introduction of this report will be described. First, the procedures currently available are reviewed.

Column testing

95. Application. Column techniques have been used in a variety of ways to simulate field leaching processes. The migration of chemical substances through soil is usually studied in this manner. For example, it may be desired to study the interaction of leachate with underlying soils. A column is packed with a representative soil and then challenged with specific leachate. The laboratory apparatus is similar to that shown in Figure 7. Samples are collected and analyzed at periodic intervals to determine leachate quality after passage through the soil column (Jackson, Garrett, and Bishop 1984). Data collected from column studies are usually presented as a plot of leachate quality versus the volume of liquid passing through the column. Sometimes the cumulative volume is represented by the number of pore volumes that have passed through the bed. The curves are usually interpreted as relevant simulations of leachate quality under field conditions. The similarity between the laboratory column and actual field conditions can readily be seen.

96. Column flow regimes. Flow regimes in leaching columns can be divided into two idealized classes. These are "plug flow" and "back-mix flow." Plug flow is visualized as a plug moving along a prescribed path. Lateral mixing is allowed, but no longitudinal mixing is permitted. A visual model of this type system is shown in Figure 8. Back-mix flow may be either batch or continuous. An idealized back-mix reactor is instantaneously and completely mixed. Contents of the reactor volume are homogeneous throughout. These systems are sometimes called "complete-mix" flow. This type of system is depicted in Figure 9. In a leaching column, flow is probably a combination of these two systems, as shown in Figure 10. If the leaching column is

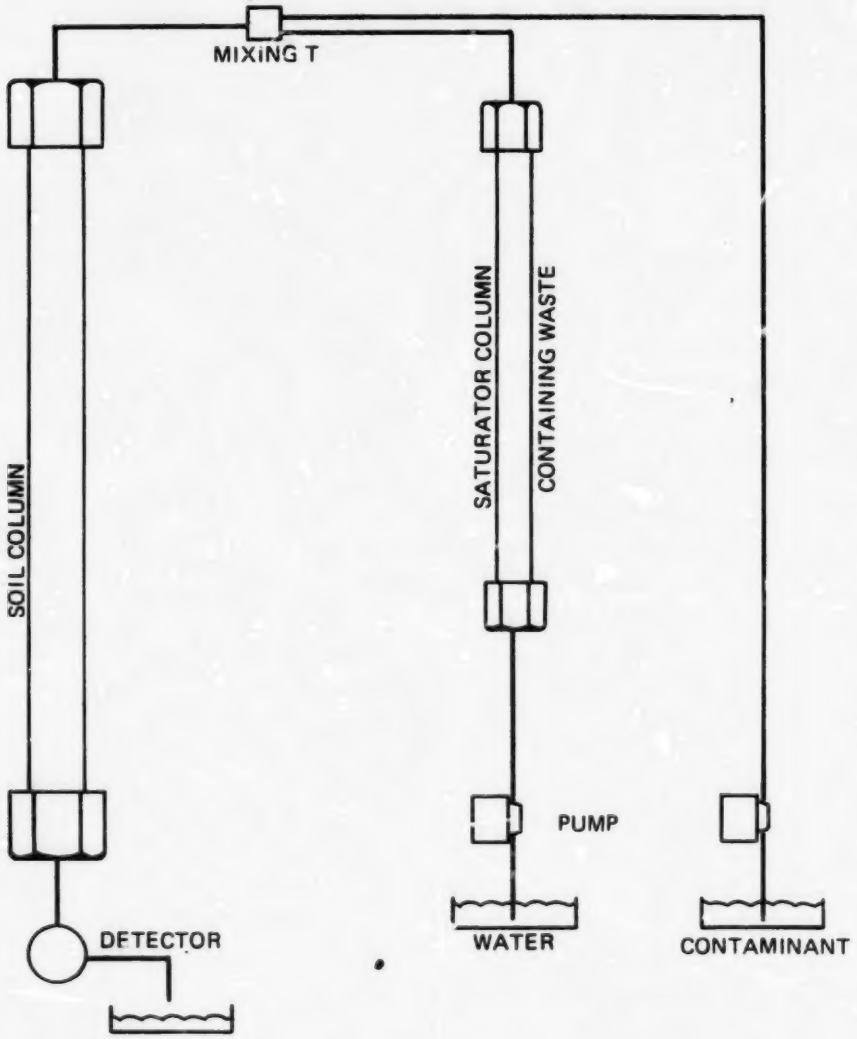

Figure 7. Typical column test apparatus for soil attenuation studies

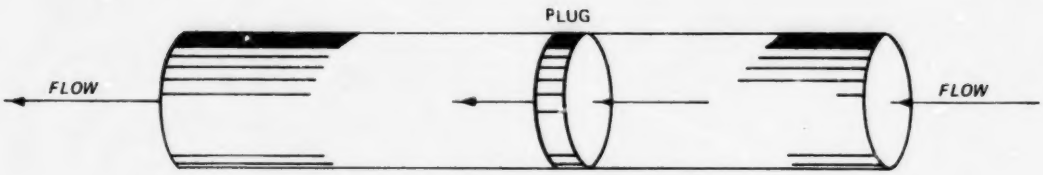

Figure 8. Plug flow reactor model

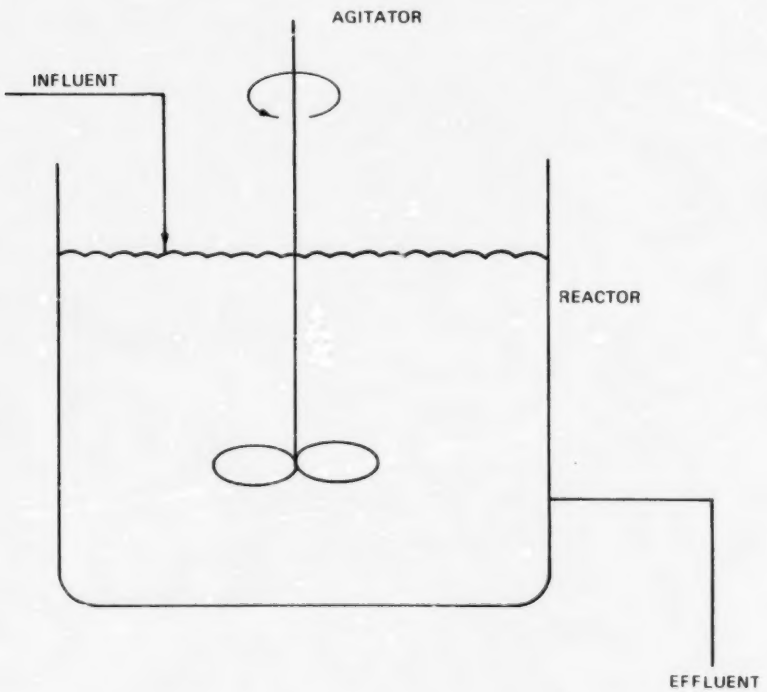

Figure 9. Back-mix reactor model

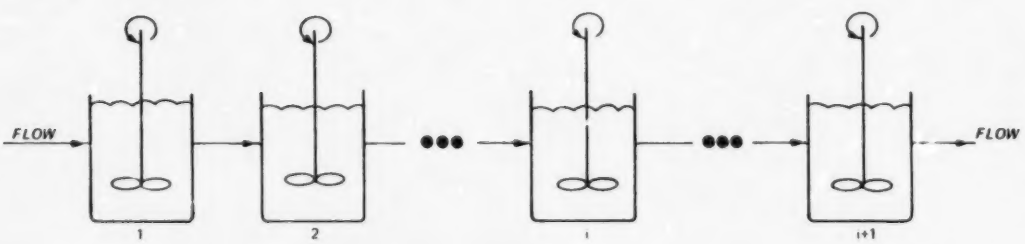

Figure 10. Back-mix reactors in series

considered to be a finite number of finite-sized back-mix reactors of sufficient number and size, the flow will approach plug flow conditions. This principle is the basis for interpretation of column leaching data.

97. Even though column studies provide useful data, there are definite limitations. One limitation of column tests is the time required to obtain the desired number of samples. To gain sufficient information to make predictions of leaching rates, the time frame may be months or years if a gravity column is used. Column flows are often so small that the amount of sample needed for chemical analysis is difficult to obtain. Static pressure can be applied to increase the flow rate. But even with pressure, the fluid velocity is very small.

98. Operationally, column tests, particularly gravity columns, have limitations that can seriously compromise the utility of the data. For small-diameter columns, side wall effects can be important. Since fluid flow in the field situation is gravity flow, gravity columns are usually used. Gravity columns are difficult to saturate and, as a consequence, channeling within the bed can lead to seriously misleading leaching rates (Jackson, Garrett, and Bishop 1984). Pressurized columns yield higher flow rates, can be saturated, and can be operated anaerobically. However, the simulation of field conditions obtained may be questionable.

Batch testing

99. Description. The apparatus and testing procedures for batch testing are more varied than for column testing (Lowenbach 1978, Conway and Malloy 1981, Conway and Gulledge 1983). Batch reactors have varied from mason jars to agitated tanks. Separatory funnels and Erlenmeyer flasks have also been used. Mixing has been provided by electric mixers, shakers of various configurations, and simple manual shaking. Solvents utilized as the extractant have included tap water, deionized water, and additives such as hydrochloric acid, carbon dioxide, acetic acid, glycol, glycerine, and caustic have been used for pH adjustment. Reaction periods vary from 30 min to 24 hr typically at ambient temperature.

100. Batch testing procedures evolved for almost a decade before standardization was attempted. The Japanese government appears to have been the first to adopt batch testing (Lowenbach 1978, Perket and Webster 1981). The Japanese procedure employed continuous agitation for 6 hr at a pH between 5.8 and 6.3. The dilution ratio was 10:1 and temperature was ambient. Hydrochloric

acid, CO_2, or sodium hydroxide was used to adjust the pH to the proper range. Phase separation was by centrifugation and filtration.

101. The Corps of Engineers researched and developed a batch procedure known as the Elutriate Test (Lee and Plumb 1974). This test was designed specifically for evaluating the release of contaminants from dredged materials during open-water disposal (US Environmental Protection Agency (USEPA) 1980a, 1980b). The elutriate test uses a liquid/solid ratio of 4:1, an agitation period of 30 min, and 1 hr settling. The liquid phase is decanted and filtered through a 0.45-μ filter. The test has been modified and used to assess water quality impacts of ponded water discharged from CDF's during active dredging (Palermo 1986).

102. Several states developed their own batch test procedures (Lowenbach 1978). The Minnesota Pollution Control Agency used a distilled water method at a dilution ratio of 40:1. The dilution ratio was later reduced to 4:1. Acetic acid was used to adjust the pH to 4.5. The reactor was a separatory funnel, and the batch was mixed at initiation and once at termination of the test. The Illinois EPA test used deionized water, a variable dilution ratio, and hydrochloric acid and/or caustic to adjust the pH to 6.0 (Lowenbach 1978). The dilution ratio was a constant 4:1, and agitation was provided by a reciprocating shaker. Other states that developed their own procedures include Indiana, New Jersey, Michigan, Pennsylvania, and Texas (Lowenbach 1978).

103. The first attempt to develop a standard test method for hazardous waste was carried out at the University of Wisconsin on behalf of the USEPA (Ham et al. 1979). From this work came the Standard Leach Test (SLT) which used a dilution ratio of 10:1. The extractant was either water or a mixture comprised of acetic acid and a buffered solution containing glycerine, pyrogallol, and ferrous sulfate. Multiple extractions were carried out at ambient temperature. Agitation was carried out by rolling the bottles for a 24-hr period. Eventually the SLT evolved into the EPA's Toxic Extraction Procedure (EP) (USEPA 1980c). The latest version of the EP is directed to the classification of wastes as hazardous or nonhazardous based upon their leaching potential under standard conditions.

104. Batch test procedures have all been criticized (Conway and Malloy 1981, Conway and Gulledge 1983). Lee and Jones (1981) have criticized the EP procedure on the basis of inattention to oxidation-reduction potential. Lee and Jones (1981) contended that chemical characteristics of the leaching

environment are the most important factors governing the release of contaminants from solid wastes. Specifically, they contend that most of the batch procedures are not responsive to site-specific factors that are important in the field situation.

105. Field application. It is realized that a number of test conditions, such as pH, oxidation-reduction potential, solid/liquid ratio, and type of extractant, will affect the outcome of a test. However, field extrapolation of laboratory leachate data involves more than the selection of test conditions. There must be a technical basis, either empirical or deterministic, on which to extrapolate to the field situation. In an empirical approach, laboratory data are compared directly to field data. The necessary adjustments are made in the important parameters of the laboratory test until the laboratory data begin to agree with the field data. In a deterministic approach, a test is designed to reveal important information about the physical-chemical laws governing a system. This information is then used in a mathematical description of the problem to predict the field situation. Comparison is made between predicted and observed, and the theoretical model is either refined or abandoned.

106. The basic philosophy behind the EP is somewhere between these two classifications. It is a criteria-comparison type test developed out of regulatory necessity for a fast, uncomplicated, standardized procedure. EP leachate is compared to a set of specific concentration limits for selected contaminants. This provides the basis for classifying a waste as hazardous or nonhazardous.

107. The EP leach test, however, is not suitable for describing the source term in Equation 2. It does not provide information on leaching kinetics or on equilibrium desorption coefficients for the solid and aqueous phases. The EP data should correlate to the field situation in some way, but correlation functions have not been established. The utility of the EP as a direct simulation of the field situation is also limited. In particular, the leachant pH, the oxidation-reduction potential, and the liquid/solid ratio used do not simulate field conditions in most situations. Hence, direct extrapolation to the field situation on the basis of similitude is usually not justified (Lee and Jones 1981).

108. The elutriate test is similar to the EP in that it is a standardized procedure that is fast and uncomplicated. Unlike the EP, it was designed to

simulate a specific disposal situation for a specific type of material--dredged material. Elutriate data are extrapolated to the field situation on the basis that the test simulates critical field parameters related to contaminant mobility during dredging operations. The solid/liquid ratio, mixing effort, oxidation-reduction potential, and extractant were all selected to be representative of typical dredging operations. Therefore, the elutriate test is a good simulation of the short-term impact that dredged material has on the water it is mixed with during dredging. As is the case with the EP, the elutriate test provides little information on the basic processes responsible for contaminant transfer from dredged material solids to the aqueous phase.

109. It is apparent from the previous discussions of distribution coefficients, desorption isotherms, film effects, and kinetics that a single batch extraction cannot provide the information needed for predicting contaminant leaching using a mass transport equation. As previously discussed, leaching is a complex process involving convection, dispersion, and contaminant transfer from the dredged material solids into the aqueous phase. It is not likely that simple procedures and approaches will adequately simulate the process.

Recommended Test Procedures

Accelerated testing

110. Accelerated testing is mandatory for dredged material research. If testing times approach those of the natural setting, there is little practical use for the results. Leaching tests may be accelerated by modifying conditions of the test so as to enhance the leaching rate. Several methods accelerate leaching by maximizing the driving forces. These methods include:

a. Testing at high temperature.

b. Increasing the leachant velocity.

c. Adjusting the pH, redox potential, and ionic strength.

The major difficulty in accelerated testing has to do with interpretation of data. This is particularly true for items a and c. High temperatures may cause irreversible changes in sediment characteristics. Organics with high vapor pressure may be desorbed and expelled from the system. Inorganics such as carbon dioxide, hydrogen sulfide, and perhaps others could be lost to the atmosphere. These factors would likely alter pH, redox potential, and certainly ionic strength.

111. Intentional adjustments in pH, Eh, and ionic strength are surely the most stringent and artificial. For example, an acidic pH in the range of 3.5 to 4.5 would likely improve the sorption of organic compounds that have carboxlyic acid groups due to a shift in equilibrium. At the same time, some metal ions would become more soluble and some less soluble. The ionic strength would also be increased, which in turn would decrease activity coefficients. Oxidation-reduction potentials would be altered, as well as charge densities on contaminant adsorption sites on the dredged material. Additions of organic acids to adjust pH may react irreversibly with some metal ions. For example, acetic acid is a recognized chelating agent for metals such as chrome (III) (Stumm and Morgan 1981). Strong mineral acids may react with organics or cleave chains through hydrolysis. If the purpose is to determine the total concentration of adsorbed metal ions, then a strong mineral acid is in order. If the objective is to predict leaching conditions in a natural environment, test conditions must be maintained that do not significantly alter chemical and physical parameters (Lowenbach 1978).

112. It would appear that item b is the most likely candidate for accelerated testing. The functional dependence of the leach rate on the leachant velocity can be used to obtain accelerated leaching data that can be related to the leach rate under field conditions (Cote 1986). The major difficulty that may arise is justifying the assumption that leaching under both accelerated and field conditions is governed by the same processes. However, the objectives of any study and the intended end use of the data must be clearly understood before test methods are selected. If the intended use is for predicting long-term field conditions, only item b should be considered.

Batch testing

113. Batch tests are rapid compared to column tests because, in a batch test, the renewal rate of leachant at the sediment surface is virtually infinite compared to renewal rate in a column test. By relating the volume of liquid used in a batch test to the percolation rate in a CDF, sequential batch extractions can be the basis of an accelerated testing protocol (Houle and Long 1980; Van der Sloot, Piepers, and Kok 1984). A modification of the sequential batch testing approach of Houle and Long (1980) and Garrett et al. (1984) is recommended for obtaining equilibrium-distribution coefficients for the source term. The assumption is made that contaminant leaching is equilibrium controlled for contaminants that are not solubility limited. This

assumption is justified on the basis that the rates at which desorption proceed are fast in relation to the rate at which water percolates through the dredged material. The procedure uses the same volume of leachant for successive extractions rather than increasing the water-to-sediment ratio with each successive extraction (grading). This procedure will directly infer the long-term leaching response afforded by the approach of Houle and Long (1980) but will avoid changes in water-to-sediment ratios that can adversely affect the field applicability of laboratory-derived distribution coefficients.

114. A sediment sample is challenged with successive aliquots of distilled water. Phase separation is accomplished by centrifuging the sample at 6,000 to 10,000 rpm followed by filtration through a 1.0-μ glass fiber filter for organic constituents and through a 0.45-μ membrane filter for metals prior to chemical analysis of the leachant. The data will be used to plot a desorption isotherm such as shown in Figure 3. From this plot an assessment of the linearity and reversibility of the desorption process can be made. If the process is linear, the slope of the line is the distribution coefficient needed in the equilibrium source term. A nonlinear plot suggests that other source terms should be evaluated.

115. Batch tests will be conducted under both anaerobic and aerobic conditions to simulate the range of conditions found in CDF's. For anaerobic testing, all steps in the procedures will be conducted under a nitrogen gas atmosphere. For aerobic testing, the sediment will be incubated to allow oxidation by exposure to the air and natural drying by evaporation to give a moist, manageable, aerobic sediment. This oxidation process will be allowed to proceed for up to 6 months to permit physicochemical changes caused by oxidation to occur.

116. The situation in which leachate moves from the upper oxidized zone of a CDF into a lower reduced zone will also be simulated. This will involve challenging anaerobic sediment with leachate from aerobic sediment. Successive aliquots of both aerobic and anaerobic sediment will be challenged by leachate from a previous aliquot. These data will be used to determine distribution coefficients suitable for predicting leachate quality in a CDF that contains anaerobic sediments covered by an oxidized layer, and a CDF containing completely aerobic dredged material.

117. Other associated testing procedures must also be conducted prior to initiation of the sequential batch leaching test. This testing will determine

shaking time and sediment-to-water ratios to use during testing. To determine the time necessary for soluble contaminant concentrations to stabilize at "steady-state" values, kinetic tests will be conducted. These tests involve shaking sediment and water and sampling soluble contaminant concentrations over time. Such testing will indicate whether the assumption of equilibrium between leachate and sediment is valid. Such tests will also provide information on kinetic processes if the system is not equilibrium controlled. It is also mandatory that the effect of the solid-to-liquid ratio on the value of the partition coefficient be evaluated. Solid/liquid ratios in the range from 1:1 to 10:1 will be investigated in order to identify the highest sediment-to-water ratio that can be used without compromising the validity of the partition coefficients. This testing will be conducted both independently of and within the context of the sequential batch leach testing.

Column testing

118. Pressurized column testing will be conducted to provide a laboratory-scale, physical model of the field situation. Divided-flow permeameters developed by Anderson (1983) for investigating leachate interactions with landfill liners will be used. The double-ring design minimizes errors in calculating leaching rates that are caused by side wall effects. The system can be saturated with back pressure to eliminate channeling, and it can be operated under anaerobic conditions by using deoxygenated water as a leaching medium. The system is pressurized so that the applied head can be varied as needed to increase flow. Using this technique, long-term leaching can be simulated on an accelerated time scale.

119. The quality of the permeameter effluent will be measured. The change in leachate quality with time (pore volumes passed) represents the accumulation term, $\partial C/\partial t$, in Equation 1. Coefficients for the bulk flow and dispersion terms will be measured directly. Bulk flow will be based on Darcy permeability (Anderson 1983), and column dispersion will be determined by passing a conservative tracer through the permeameter (Levenspiel 1972). Since the accumulation, bulk flow, and dispersion terms can be determined for the sediment column in the permeameter, permeameter testing can be used to analyze the source term (Goerlitz 1984). The techniques for this type of analysis are still experimental, and additional work will be needed before column tests alone can be used to mathematically describe the fundamental processes responsible for the source term.

Correlating batch and
column desorption studies

120. Houle and Long (1980) postulated that a continuously leached column is equivalent to running a series of discrete extractions spaced by the frequency of collecting the effluent sample. Each extraction in a series represents an equivalent volume of leachate percolating through a CDF. Sequential batch extractions produce a curve similar to that shown in Figure 11. A curve of the same form is produced by a continuously leached column of the same sediment. The assumption is made that the contaminant concentration in each batch extraction represents the leachate quality for passage of an equivalent number of pore volumes of water. Thus, sequential batch data, as discrete points on a continuous curve, can be graphically compared to the discrete data from a continuously leached column. If the match is good, then dispersion, kinetics, and film effects can be disregarded.

121. Goerlitz (1984) and Grove and Stollenwerk (1984) have used batch and/or column tests in combination with a mass transport equation to model adsorption and transport of contaminants in ground-water systems. The equilibrium distribution coefficients determined in batch testing are used in conjunction with the column dispersion coefficient and Darcy velocity to construct a leachate quality versus pore volume curve using Equation 1. If the predicted curve matches the curve from the column, the inference can be made that the equilibrium approach is satisfactory and that Equation 1 can be used to predict leachate quality. In general, batch data, column data, and mass transport equations can thus be integrated to provide information on probable leachate quality in CDF's for dredged material.

122. For application of the proposed mass transport equation to the field situation, site-specific information will be needed on field conditions. Often the application of a mass transport equation to a real situation may be very complex. Difficulty usually manifests as inability to accurately describe initial and/or boundary conditions, reaction mechanisms, and the way in which these terms change with time. In the case of contaminant leaching from dredged material in a CDF, it is a question of carrying out a laboratory program that yields meaningful data within an acceptable time frame. The laboratory program recommended in this report involves a state-of-the-art attempt to provide quantitative description of the source term in a mass transport

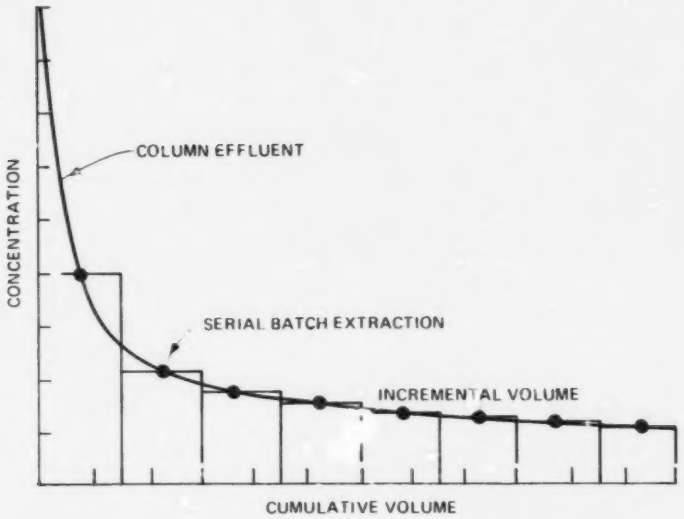

Figure 11. Correlation of serial batch and column leaching data

equation. It is designed to yield meaningful data (data that can be extrapolated to the field situation) in an acceptable time frame.

PART VI: SUMMARY

123. A one-dimensional mass transport equation was developed for analyzing contaminant transport in a dredged material confined disposal facility. The equation combines convective-diffusive transport with leaching of contaminants from dredged material solids. The mass transport equation is given as follows:

$$\frac{\partial C}{\partial t} + \frac{\rho}{\theta} \frac{\partial q}{\partial t} = D_p \frac{\partial^2 C}{\partial z^2} - v \frac{\partial C}{\partial z} \qquad (39)$$

The source term, $\partial q/\partial t$, depends on the fundamental processes controlling contaminant transfer from the dredged material solids to the aqueous phase. Assuming that attendant boundary and initial conditions can be described, the above equation may be used to develop planning level assessments of leachate quality and leachate generation rate in a confined disposal site.

124. The source term was conceptualized as desorption of contaminants from the solid phase into the aqueous phase. Various approaches to describing desorption were considered, including both equilibrium and nonequilibrium processes. The simplest, most often used, and the one recommended for investigation first is the equilibrium approach. The equilibrium approach uses a simple distribution (partition) coefficient to relate aqueous phase concentration to solid phase concentration.

125. State-of-the-art leaching procedures were reviewed for potential application to dredged material. Various topics related to sediment chemistry impacts on leaching processes were also reviewed. A sequential batch leaching procedure is recommended for obtaining the coefficients needed in the mass transport equation. In order to verify the equilibrium assumption and the mass transfer equation, a pressurized column test using divided-flow (double-ring) permeameters is recommended as a physical model of reduced scale.

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APPENDIX A: DERIVATION OF ONE-DIMENSIONAL MASS TRANSPORT EQUATION

1. In this appendix, a derivation for Equation 1 is presented. (Reference is made to Figure 1 of the main text.) For the volume element shown, the principle of conservation of mass applies to the sediment solids, the percolating fluid (leachate), and the contaminants dissolved in the fluid and associated with the sediment solids. The conservation of mass in the z-direction is given by

$$\begin{bmatrix}\text{Rate of}\\ \text{Mass In}\end{bmatrix} - \begin{bmatrix}\text{Rate of}\\ \text{Mass Out}\end{bmatrix} = \begin{bmatrix}\text{Rate of Mass}\\ \text{Accumulation}\end{bmatrix} \qquad \text{(A1)}$$

2. Individual terms for Equation A1 are as follows:

Rate of mass in

Bulk flow across plane at $z = (vC)\Delta x\Delta y\Big|_z$

Dispersion across plane at $z = - D_p \frac{\Delta C}{\Delta z} \Delta x\Delta y\Big|_z$

Rate of mass out

Bulk flow across plane at $z + \Delta z = (vC)\Delta x\Delta y\Big|_{z+\Delta z}$

Dispersion across plane at $z + \Delta z = - D_p \frac{\Delta C}{\Delta z} \Delta x\Delta y\Big|_{z+\Delta z}$

Mass accumulation rate

Mass accumulation rate, solid phase $= \frac{\rho}{\theta} \frac{\Delta q}{\Delta t} \Delta x\Delta y\Delta z$

Mass accumulation rate, aqueous phase $= \frac{\Delta C}{\Delta t} \Delta x\Delta y\Delta z$

Variable C refers to the aqueous phase contaminant concentration; q refers to the solid phase contaminant concentration; v refers to the average fluid velocity in the z-direction; D_p is the hydrodynamic dispersion coefficient; ρ is the solids density of the volume element; θ is the volumetric water content; and x, y, and z are as defined in Figure 1 of the main text.

3. When these individual terms are substituted into Equation A1, the following result is obtained:

$$(vC)\Delta x\Delta y\Big|_z - (vC)\Delta x\Delta y\Big|_{z+\Delta z} - D_p \frac{\Delta C}{\Delta z}\Delta x\Delta y\Big|_z + D_p \frac{\Delta C}{\Delta z}\Delta x\Delta y\Big|_{z+\Delta z} = \frac{\Delta C}{\Delta t}\Delta x\Delta y\Delta z + \frac{\rho}{\theta}\frac{\Delta q}{\Delta t}\Delta x\Delta y\Delta z \qquad (A2)$$

4. Dividing by $\Delta x\Delta y\Delta z$ yields

$$\frac{(vC)\Big|_z - (vC)\Big|_{z+\Delta z}}{\Delta z} + \frac{-D_p \frac{\Delta C}{\Delta z}\Big|_z + D_p \frac{\Delta C}{\Delta z}\Big|_{z+\Delta z}}{\Delta z} = \frac{\Delta C}{\Delta t} + \frac{\rho}{\theta}\frac{\Delta q}{\Delta t} \qquad (A3)$$

5. Taking the limit as Δ approaches zero, the following partial differential equation is obtained:

$$-\frac{\partial (vC)}{\partial z} + \frac{\partial D_p \frac{\partial C}{\partial z}}{\partial z} = \frac{\partial C}{\partial t} + \frac{\rho}{\theta}\frac{\partial q}{\partial t} \qquad (A4)$$

6. Taking v and D_p to be constant

$$\frac{\partial C}{\partial t} + \frac{\rho}{\theta}\frac{\partial q}{\partial t} = D_p \frac{\partial^2 C}{\partial z^2} - v\frac{\partial C}{\partial z} \qquad (A5)$$

Equation A5 is Equation 1 of the main text. It is a one-dimensional partial differential equation that accounts for conservation of mass in the aqueous and solid phases. It is assumed that solids density in the volume element is constant, i.e., consolidation is not accounted for.

7. The source term, $\partial q/\partial t$, is conceptualized as transfer of contaminant from the solid phase to the aqueous phase. The solids density of the volume element and the volumetric water content are used to express a decrease in solid phase concentration as leaching by percolating water. In the main body of the text, $\partial q/\partial t$ is referred to as the source term denoted by "S."

APPENDIX B: FUGACITY BASIS FOR EQUILIBRIUM DISTRIBUTION COEFFICIENTS

1. In this appendix an expression for a thermodynamically rigorous distribution coefficient is developed using fugacity principles. Such derivations are important in understanding the theory of equilibrium. The remainder of the appendix is devoted to describing the phenomenally based distribution coefficient that is determined using sequential batch leach procedures, as well as further defining some of the terminology associated with equilibrium coefficients used in this report.

2. The following discussion is taken from the works of Thibodeaux (1979) and Mackay (1979). For isothermal conditions, changes in chemical potential are related to changes in fugacity. Fugacity may be expressed as a function of the chemical activity coefficient, (γ), mole fraction (X), and a reference fugacity for the contaminant of interest (f^o). Fugacity is defined as follows:

$$(f_i)_j = (\gamma_i X_i f_i^o)_j \tag{B1}$$

where the subscript j refers to the phase (1 = air, 2 = water, 3 = sediment) and i refers to the i^{th} contaminant. Interphase equilibrium is established when the contaminant fugacities in the solid and aqueous phases are equal, that is

$$(\gamma_i X_i f_i^o)_2 = (\gamma_i X_i f_i^o)_3 \tag{B2}$$

3. Fugacity can be regarded as the escape tendency of a contaminant from a phase (Mackay 1979). If the aqueous phase fugacity is less than the solid phase fugacity, a net transfer of contaminant to the aqueous phase will take place. As long as Equation B2 is satisfied, significant differences in phase concentrations can exist and be in equilibrium.

4. Rearrangement of Equation B2 yields

$$X_{i3} = \frac{X_{i2}(\gamma_{i2} f_{i2}^o)}{\gamma_{i3} f_{i3}^o} \tag{B3}$$

If $\gamma_{i2}f^{o}_{i2}$ = a constant and $\gamma_{i3}f^{o}_{i3}$ = a constant, the distribution coefficient, K_d, defined below will be constant.

$$K_d = \frac{\gamma_{i2}f^{o}_{i2}}{\gamma_{i3}f^{o}_{i3}} \tag{B4}$$

5. The product of the activity coefficient, γ, and the reference fugacity, f^{o}, is called the fugacity product and is denoted as γf^{o}. For K_d to be constant, it is necessary that the phase fugacity products be in a constant ratio. Equation B3 can now be written as

$$X_{i3} = K_d X_{i2}$$

or

$$K_d = \frac{X_{i3}}{X_{i2}} \tag{B5}$$

6. The mole fractions in Equation B5 can be replaced by mass fractions, W, without any loss of generality so that Equation B5 can be written as

$$K_d = \frac{W_{i3}}{W_{i2}} \tag{B6}$$

where W_{i3} is the mass fraction of the i^{th} chemical species in the sediment and W_{i2} is the mass fraction of the i^{th} chemical species in the aqueous phase. Concentration can be substituted for mass fraction so that Equation B6 becomes

$$K_d = \frac{q}{C} \tag{B7}$$

where q is the solid phase concentration and C is the aqueous phase concentration.

7. The partition coefficient, K_d, is often defined as it is written in Equation B7. The proper definition is given by Equation B4. As a practical matter, K_d is most easily measured using Equation B7. There is a subtle but important difference between Equations B4 and B7. The thermodynamics of the system do not imply that at equilibrium the phase concentrations will always be at a constant ratio. The only guarantee provided by thermodynamics is that, at equilibrium, the phase fugacities will be equal as per Equation B2. It should not be surprising, then, to find that K_d is variable, depending on phase physical-chemical characteristics (reference fugacity) and the chemical activity of the contaminant (γ). If these quantities vary during the conduct of an isotherm test, K_d as defined in Equation B4 is not likely to remain constant.

8. The above discussion was concerned with thermodynamically rigorous equilibrium or distribution coefficients because a key step in the derivation is the assumption of interphase equilibrium in Equation B2. As a practical matter, however, it is difficult if not impossible to determine when a solid phase/aqueous phase system has actually reached the condition dictated by Equation B2. Thus, when attempting to determine equilibrium values of $q + C$ in the lab, a phenomenalistic definition of equilibrium is normally adopted. This simply means that within any step in a sequential shake test, equilibrium is assumed when measured values of C stop changing. The period of time beyond which q and C do not change within a step is often used to characterize the procedure. For instance, a 24-hr distribution coefficient implies that q and C did not change beyond a 24-hr shake period within each step in the procedure.

9. The terms partition coefficient, K_p, and distribution coefficient, K_d, are often used interchangeably. Current literature offers no clear distinction in usage. In this report, K_p generally refers to the distribution of organic compounds whereas K_d generally refers to distribution of nonorganic materials.

APPENDIX C: DEVELOPMENT AND USE OF ADSORPTION ISOTHERM EQUATIONS

Freundlich Isotherm

1. A simple adsorption/desorption kinetic model, based on mass action, is given below.

$$\frac{dq}{dt} = -K_F q + K_R C \qquad (C1)$$

where K_F is the rate constant for desorption, K_R is the rate constant for adsorption, C is the mass concentration of contaminant in the aqueous phase, and q is the mass concentration of contaminant in the solid phase. At equilibrium

$$\frac{dq}{dt} = 0$$

and Equation C1 becomes

$$\frac{K_R}{K_F} = \frac{q}{C}$$

2. Letting $K_d = K_R/K_F$, we have

$$K_d = \frac{q}{C} \qquad (C2)$$

Equation C2 is equivalent to Equation B7. A useful form of Equation C2 is

$$q = K_d C \qquad (C3)$$

3. Equations of this form satisfactorily model the linear portion of the curve shown in Figure 2 of the main text. When the sorbent begins to approach its limiting capacity, simple equations no longer fit. Equation C3 can be

adjusted to accommodate the curved region by writing a slightly different kinetic equation

$$\frac{dq}{dt} = -K_F q + K_R C^{1/n} \qquad \text{(C4)}$$

where $1/n$ is an empirical coefficient used to provide a better fit to a particular set of data. At equilibrium

$$\frac{dq}{dt} = 0$$

and Equation C4 becomes

$$q = \left(\frac{K_R}{K_F}\right) C^{1/n} \qquad \text{(C5)}$$

4. This is the Freundlich isotherm equation. The Freundlich partition coefficient is defined as

$$K_{pf} = \frac{K_R}{K_F} = \frac{q}{C^{1/n}} \qquad \text{(C6)}$$

5. The Freundlich isotherm is an empirical model that was developed for a special case of heterogeneous surface energies in which the partitioning coefficient varies as a function of surface coverage. It should be noted that when $n = 1$ in Equation C6, the equation is linear. In addition, it is equivalent to the linear form of the Langmuir equation discussed below.

Langmuir Isotherm

6. In 1918, Langmuir proposed an adsorption model for a gas-solid interface. The model assumes uniform adsorption energy, constant heat of adsorption, a saturated monolayer on the surface, and the absence of transmigration of sorbate in the sorbent. By including a capacity factor for the sorbent and expressing the adsorption side of the sorption process as a function of both

aqueous phase concentration and the difference between sorbent ultimate capacity and the amount of sorbate actually sorbed, the Langmuir model predicts an asymptotic approach to some empirically determined ultimate sorbent capacity. Thus, the Langmuir isotherm provides good fit to adsorption data and provides a rational basis for the form of the curve that the data follow. Even though the equation was originally derived for the adsorption of gases on solids, it is often used for modeling adsorption of contaminants from wastewater. The Langmuir equation is as follows:

$$\frac{dq}{dt} = K_R C(Q_o - q)M - K_F qM \qquad \text{(C7)}$$

where

K_R = rate constant for adsorption
C = mass concentration in the aqueous phase
Q_o = ultimate adsorbent capacity (monolayer) of the sorbent
q = mass concentration in the sorbent phase
M = mass of sorbent
K_F = rate constant for desorption

7. For $dq/dt = 0$, Equation C7 becomes

$$K_R C(Q_o - q) = K_F q$$

or

$$q = \frac{\frac{K_R}{K_F}(Q_o C)}{1 + \frac{K_R}{K_F} C} \qquad \text{(C8)}$$

8. Equation C8 is the Langmuir isotherm equation. A Langmuir partitioning coefficient can be defined as

$$b = \frac{K_R}{K_F}$$

so that Equation C8 can be written as

$$q = \frac{bQ_o C}{1 + bC} \tag{C9}$$

9. Rearranging Equation C9 yields

$$b = \frac{q}{C(Q_o - q)} \tag{C10}$$

Hence, the Langmuir partitioning coefficient is neither dimensionless nor simply a ratio of aqueous phase mass fraction (concentration) to sorbed phase mass fraction (concentration).

10. A second form of the Langmuir isotherm equation occurs where the adsorbed concentration is very small. In this case, bC is much less than unity. The Langmuir equation becomes a linear equation describing the linear portion of the plot of q versus C.

$$q = Q_o bC \tag{C11}$$

11. A third relationship develops where large amounts of adsorption occur. In this case, bC is much greater than 1 and the equation becomes

$$q = Q_o \tag{C12}$$

BET Isotherm

12. The Brunaer-Emmett-Teller (BET) isotherm was developed for multiple-layer adsorption. Since in natural systems the extent of adsorption is usually one or more orders of magnitude less than the capacity of the adsorbent, the BET has not found application in these systems.

APPENDIX D: DEVELOPMENT AND USE OF DESORPTION ISOTHERM EQUATIONS

1. One desorption isotherm would be the simple adsorption isotherm equation developed in Appendix C (Equation C3).

$$q = K_d C \tag{D1}$$

This isotherm equation describes the relationship between sorbed and aqueous phase concentrations at equilibrium for a completely reversible system. If a residual, irreversibly adsorbed fraction is present on the sediment, then Equation D1 below applies.

$$q = K_d C + q_r \tag{D2}$$

where q_r = residual mass concentration of the solid phase that cannot be leached .

2. An aqueous phase solubility limit may apply for some contaminants. The desorption kinetics for this situation are given below.

$$\frac{dq}{dt} = K_R C - K_F(C_s - C)(q - q_r) \tag{D3}$$

where C_s = aqueous phase solubility limit .

3. At equilibrium, dq = dt and Equation D2 becomes

$$\frac{dq}{dt} = 0$$